



This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

### Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

- + *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.
- + *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.
- + *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.
- + *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

### About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at <http://books.google.com/>

KB.1 129

HARVARD UNIVERSITY



LIBRARY OF THE  
BIOLOGICAL LABORATORIES

*From*  
HARVARD COLLEGE LIBRARY

MAY 4 1949







THE JOURNAL  
—OF THE—  
AMERICAN CHEMICAL SOCIETY.

---

VOLUME XVII.  
1895.

---

COMMITTEE ON PAPERS AND PUBLICATIONS:

EDWARD HART, Editor,  
J. H. LONG,  
THOMAS B. OSBORNE.

Photolithograph Reproduction  
By Permission of The American Chemical Society

JOHNSON REPRINT CORPORATION  
NEW YORK, N. Y., U. S. A.

Δ

KGA 129

✓



---

COPYRIGHT, 1895,

BY EDWARD HART, JOHN H. LONG,  
AND THOMAS B. OSBORNE.

Committee on Papers and Publications of the  
American Chemical Society.

---

PHOTOLITHOGRAPHED BY  
THE MURRAY PRINTING COMPANY  
WAKEFIELD, MASSACHUSETTS

# Contents of Vol. XVII, 1895.

## PROCEEDINGS.

### JANUARY.

New Members Elected November 30.....	(1)
“ “ “ December 10.....	(1)
Changes of Address.....	(2)
Meetings of the Sections—	
New York Section .....	(2)
Washington Section.....	(3)

### FEBRUARY.

Annual Meeting of the American Chemical Society .....	(5)
Council.....	(21)
New Members Elected December 26.....	(21)
“ “ “ January 12.....	(21)
“ “ “ January 17.....	(22)
Associates “ January 17.....	(22)
Changes of Address .....	(23)
Addresses Wanted.....	(23)
Meetings of the Sections—	
Washington Section .....	(23)
Cincinnati Section.....	(25)
Lehigh Valley Section.....	(26)

### MARCH.

Council .....	(27)
Changes of Address .....	(27)
Meetings of the Sections—	
Cincinnati Section.....	(27)
Rhode Island Section .....	(28)

### APRIL.

Council .....	(29)
New Members Elected February 5.....	(29)
“ “ “ March 1.....	(30)
Associates February 5.....	(30)
Changes of Address.....	(30)
Meetings of the Sections—	
Cincinnati Section.....	(31)
Rhode Island Section .....	(32)

### MAY.

Board of Directors.....	(33)
New Members Elected March 22.....	(33)
Changes of Address.....	(33)
Meetings of Sections—	
Cincinnati Section.....	(34)
Washington Section.....	(35)

**JUNE.**

Board of Directors .....	(37)
Council .....	(37)
New Members Elected April 8 .....	(37)
Associates " April 8 .....	(38)
New Members Elected April 9 .....	(38)
" " " 19 .....	(38)
Changes of Address .....	(38)
Meetings of Sections—	
New York Section .....	(38)
Washington Section .....	(40)
Cincinnati Section .....	(42)

**JULY.**

Council .....	(43)
New Members Elected April 29 .....	(43)
" " May 16 .....	(43)
Associates " May 16 .....	(43)
Changes of Address .....	(44)
Meetings of the Sections—	
Lehigh Valley Section .....	(44)

**AUGUST.**

Council .....	(45)
New Members Elected June 6 .....	(45)
Changes of Address .....	(45)
Meetings of the Sections—	
Rhode Island Section .....	(46)
Cincinnati Section .....	(48)

**SEPTEMBER.**

Changes of Address .....	(49)
Meetings of the Sections—	
Chicago Section .....	(47)

**OCTOBER.**

Eleventh General Meeting of the American Chemical Society .....	(51)
New Members Elected September 21 .....	(61)
Associate " September 21 .....	(61)
Changes of Address .....	(61)
Meetings of the Sections—	
Rhode Island Section .....	(62)

**NOVEMBER.**

New Members Elected October 16 .....	(63)
Changes of Address .....	(63)
Meetings of the Sections—	
Lehigh Valley Section .....	(63)
Cincinnati Section .....	(65)
Rhode Island Section .....	(65)

**DECEMBER.**

Council .....	(67)
New Members Elected November 2 .....	(67)
Associates Elected November 2 .....	(68)
Changes of Address .....	(68)
Meetings of the Sections—	
Chicago Section .....	(68)
New York Section .....	(68)
Washington Section .....	(70)
Cincinnati Section .....	(72)

# PAPERS.

## JANUARY.

On the Behavior of Allylmalonic, Allylacetic, and Ethylidenepropionic Acids when Boiled with Caustic Soda Solutions. By John G. Spenser.....	I
The Phosphomolybdic Acid Test as Applied to Lard Analysis. By George F. Tennille.....	33
Some New Solvents for Perchromic Acid. By William M. Grosvenor, Jr .....	41
Some facts Observed in the Determination of Phosphoric Acid by the Molybdic Acid Process. By Rudolf de Roode.....	43
The Addition of Calcium Chloride to the Solution of a Fertilizer in the Determination of Potash. By Rudolf de Roode.....	46
On the Preparation of Ammonium Citrate Solution. By Rudolf de Roode.....	47
The Determination of Potash in Manures. By W. E. Garrigues.....	47
The Rapid and Accurate Analysis of Bone-black. By W. D. Horne.	51
The Asphalt Question. By S. F. Peckham.....	55
Quick Estimation of Starch. By P. L. Hibbard.....	64
Alkali and Sulphurous Acid Processes Used in the Manufacture of Starch from Corn. By Horace E. Horton.....	68
NEW BOOKS: A Text-Book of Volumetric Analysis, with Special Reference to the Volumetric Processes of the Pharmacopeia of the United States; A Text-Book of Inorganic Chemistry; Die Maschinellen Hilfsmittel der chemischen Technik; The Elementary Nature of Chlorine .....	69

## FEBRUARY.

A Modified Arrangement of the Elements Under the Natural Law. By F. P. Venable.....	75
The Determination of Potash in Kainite. By Rudolf de Roode.....	85
The Oxidation of Organic Matter and the Decomposition of Ammonium Salts by Aqua Regia, in Lieu of Ignition, in the Determination of Potash in Fertilizers. By Rudolf de Roode.....	86
On Certain Phenomena Observed in the Precipitation of Antimony from Solutions of Potassium Antimonyl Tartrate. By J. H. Long	87
An Examination of the Atmosphere of a Large Manufacturing City. By Charles F. Mabery.....	105
A New Form of Water-Oven and Still. By Lewis William Hoffmann and Robert W. Hochstetter.....	122
The Determination of Nickel in Nickel-Steel. By E. D. Campbell and W. H. Andrews.....	125
The Volumetric Determination of Phosphorus in Steel and Cast Iron. By W. A. Noyes and J. S. Royse.....	129
The Contributions of Chemistry to the Methods of Preventing and Extinguishing Conflagration. By Thomas H. Norton.....	137
The Action of Organic and Mineral Acids Upon Soils. By Harry Snyder.....	148

<b>NEW BOOKS: A Treatise on Industrial Photometry, with Special Application to Electric Lighting; Descriptive Inorganic General Chemistry.....</b>	<b>151</b>
--	------------

**MARCH.**

The Synthetic Food of the Future. By Harvey W. Wiley.....	155
The Determination of Phosphoric Acid. By H. Pemberton, Jr.....	178
On the Estimation of Sulphur in Pyrites. By G. Lunge.....	181
Improvement in the Manufacture of Acetone. By E. R. Squibb.....	187
Report of Committee on Atomic Weights, Published During 1894. By F. W. Clarke.....	201
Coloring-Matter in the California Red Wines. By W. D. Bigelow...	213
The Penetration Machine—An Explanation. By H. C. Bowen.....	218
<b>NOTES: Argon: A New Constituent of the Atmosphere; Calcium Sulphite Stalactites and Stalagmites.....</b>	<b>219</b>
<b>NEW BOOKS: A Text-Book of Inorganic Chemistry; Qualitative Chemical Analysis of Inorganic Substances as Practised in Georgetown College.....</b>	<b>243</b>

**APRIL.**

The Superiority of Barium Hydroxide Solution as an Absorbent in Carbon Determinations in Steel. By James O. Handy.....	247
The Contributions of Chemistry to the Methods of Preventing and Extinguishing Conflagration. By Thomas H. Norton.....	251
Note on the Estimation of Iron and Alumina in Phosphates. By K. P. McElroy.....	260
Some Practical Points in the Manufacture of Nitroglycerol. By J. E. Blomén.....	263
Methods for the Examination of Glycerol for use in the Nitroglycerol Manufacture. By G. E. Barton.....	277
Estimation of Tellurium in Copper Bullion. By Cabell Whitehead.....	280
The Use of Sulphurous Acid ( $\text{HNaSO}_3$ ) in Manufacture of Glucose Syrup and Grape-Sugar. By Horace E. Horton.....	281
The Furfurol-Yielding Constituents of Plants. By C. F. Cross, E. J. Bevan, and C. Beadle.....	286
The Separation of Solid and Liquid Fatty Acids. By E. Twitchell..	289
Improved Methods of Water Analysis. By Irving A. Bachman.....	296
A Cheap Form of Self-Regulating Gas Generator. By W.W.Andrews	304
Some of the Properties of Calcium Carbide. By F. P. Venable and Thomas Clarke.....	306
Note on the Determination of Zinc. By P. W. Shimer.....	310
On the Determination of Cane-Sugar in the Presence of Commercial Glucose. By H. A. Weber and William McPherson.....	312
On the Action of Acetic and Hydrochloric Acids on Sucrose. By H. A. Weber and William McPherson.....	320
Method of Determining Chromium in Chrome Ore. By Edmund Clark.....	327
<b>NEW BOOKS: Proceedings of the Eleventh Annual Convention of the Association of Official Agricultural Chemists; Bibliography of Aceto-Acetic Ester and its Derivatives; Report on the Extent and</b>	

# CONTENTS OF VOLUME XVII.

vii

Character of Food and Drug Adulteration; Eighth Annual Report of the Dairy and Food Commissioner of Ohio; First Annual Report of the Commissioner of Agriculture of New York; A Compilation of the Pharmacy and Drug Laws of the Several States and Territories; Kräfte der Chemischen Dynamik.....	330
NOTES: An Improvement on the "Dangler's Laboratory Lamp"; Spurting in Cupellation; A Substitute for Hydrogen Sulphide..	337

## MAY.

Henry Bradford Nason .....	339
Methods for the Determination of Manganese. By W. S. Thomas...	341
The Wet Assay for Copper. By R. S. Dulin.....	346
On the Standardization of Sulphuric Acid. By F. S. Shiver....	351
On Some Experiments in the Anthracene Series. By C. E. Linebarger .....	354
On the Reaction Between Zinc Sulphate and Potassium Hydroxide. By C. E. Linebarger.....	358
Chemical Brick for Glover Towers. By Irving A. Bachman.....	360
The Contributions of Chemistry to the Methods of Preventing and Extinguishing Conflagration. By Thomas H. Norton.....	361
A Study of the Chemical Behavior of Tungsten and Molybdenum and their Trioxides. By Charles Hatch Ehrenfeld.....	381
The Determination of Sulphur in Pyrites. A Reply to Dr. Lunge. By Thomas S. Gladding.....	397
Acidity of Glucose Syrup and Grape-Sugar. By Horace E. Horton..	402
Ash in Glucose Syrup and Grape-Sugar. By H. E. Horton .....	403
The Zimmermann-Reinhardt Method for the Determination of Iron in Iron Ores. By C. T. Mixer and H. W. DuBois .....	405
On the Manufacture of Soluble Nitrocellulose for Nitrogelatin and Plastic Dynamites. By J. E. Blomén.....	411
NEW BOOKS: Elements of Qualitative and Quantitative Chemical Analysis; Elementary Qualitative Chemical Analysis.....	419
NOTES: A New Hydrogen Sulphide Generator; Molybdenum Carbide; The Gas Contained in Uraunite; Compounds of Argon.....	420
Errata .....	422

## JUNE.

Gerhard Krüss.....	423
The Proteids of the Rye Kernel. By Thomas B. Osborne.....	429
Zirconium Sulphite. By F. P. Venable and Charles Baskerville....	448
On Some Conditions Affecting the Accuracy of the Determination of Potash as Potassium Platinichloride. By A. L. Winton.....	453
The Indirect Analysis of Mixtures Containing a Common Constituent. By Edward K. Landis .....	466
Accuracy of the Dyeing Test. By Charles S. Boyer.....	468
Absorbent Blocks. By Peter T. Austen and W. Homer Broadhurst..	472
The Volumetric Determination of Zinc and a New Indicator for Ferrocyanide. By Geo. C. Stone.....	473
Some Physical Aspects of the new Gas, Argon. The Ideal Thermometrical Substance for High Temperatures. By W. R. Quinan..	477

The Tungstates and Molybdates of the Rare Earths. By Fanny R. M. Hitchcock.....	483
Some New Laboratory Apparatus. By Ewald Sauer.....	494
NEW BOOKS: Handbuch der Stereochemie; A Text-Book of Organic Chemistry; Manual of Chemistry.....	497
NOTES: Note on a Molding-sand.....	502

## JULY.

The Decarbonization of Bone-Black. By W. D. Horne .....	503
Sulphiodide of Lead. By Victor Lehner.....	511
On the Determination of Small Quantities of Phosphoric Acid by the Citrate Method. By E. G. Runyan and H. W. Wiley....	513
An Arrangement for Washing Precipitates with Boiling Water. By Frank F. Jewett.....	517
Interpretation of Some Results in the Analysis of Extracts of Fustic. By Charles S. Boyer.....	518
The Tungstates and Molybdates of the Rare Earths. By Fanny R. M. Hitchcock.....	520
A New Table for the Qualitative Separation of the Metals of the Iron Group. By C. L. Hare.....	537
The Proteids of Barley. By Thomas B. Osborne.....	539
The Determination of Nitrogen in Fertilizers Containing Nitrates. By H. C. Sherman.....	567
On Condensation; and especially on the Condensation of Nitric Acid. By Edward Hart.....	576
Some Points in the Distillation of Nitric Acid. By Edward Hart....	580
NEW BOOKS: Cod-Liver Oil and Chemistry; The Increase in Weight of Tin and Lead on Calcination.....	584
Professor Mark Powers.....	586

## AUGUST.

The Chemical Nature of Diastase. By Thomas B. Osborne.....	587
Note on the Purification of Glucinum Salts. By Edward Hart .....	604
The Composition of the Tuberculosis and Glanders Bacilli. By E. A. de Schweinitz and Marion Dorsett.....	605
A Convenient Form of Universal Hand-clamp. By Peter T. Austen and W. A. Horton.....	611
Electrolytic Separations. By Edgar F. Smith and Daniel L. Wallace	612
On the Vapor-Tensions of Mixtures of Volatile Liquids. By C. E. Linebarger.....	615
The Electrolytic Determination of Ruthenium. By Edgar F. Smith and Harry B. Harris.....	652
The Action of Phosphorus Pentachloride Upon the Dioxides of Zirconium and Thorium. By Edgar F. Smith and Harry B. Harris..	654
NEW BOOKS: A Text-Book of Chemistry Intended for the Use of Pharmaceutical and Medical Students; John Dalton and the Rise of Modern Chemistry.....	656
Dr. Gideon E. Moore.....	659
Lothar von Meyer.....	664

## SEPTEMBER.

The Chemical History of a Case of Combined Antimonial and Arsenical Poisoning. By Charles A. Doremus, M.D., PH.D .....	667
--	-----



Action of Hydrochloric Acid Gas upon Salts of the Elements of Group V of the Periodic System. By Edgar F. Smith and Jos. G. Hibbs	682
Uranium Oxynitride and Uranium Dioxide. By Edgar F. Smith and J. Merritt Matthews	686
The Separation of Iron from Beryllium. By Elizabeth A. Atkinson and Edgar F. Smith	688
On the Vapor-Tensions of Mixtures of Volatile Liquids. By C. E. Linebarger	690
Warning Against the Use of Fluoriferous Hydrogen Peroxide in Estimating Titanium. By W. F. Hillebrand	718
The Viscosimetric Examination of Butter for Foreign Fats. By Dr. Newmann Wender	719
The Examination of Lard for Impurities. By David Wesson	723
The Action of Haloid Acids in Gas Form upon the Salts of Elements of Group V of the Periodic System. By Edgar F. Smith and Fred. L. Meyer	735
Separation of Solid and Liquid Fatty Acids. By L. de Koningh	740
Acetic Acid in Vinegar. By Albert R. Leeds	741
NEW BOOKS: An Elementary Course in Experimental and Analytical Chemistry. Elements of Mineralogy, Crystallography and Blow-pipe Analysis	744

## OCTOBER.

Ammonium Phosphomolybdate and the Reducing Action of Zinc in the Reductor. By Andrew A. Blair and J. Edward Whitfield	747
The Ferrates. By Claude A. O. Rosell	760
A Simple and Convenient Apparatus for Estimating the Water-holding Power of Soils. By J. L. Beeson	769
A Modification of Hinman's Explosion Pipette. By Augustus H. Gill	771
Estimation of Sulphur in Pyrites. By G. Lungé	772
The Periodides. By A. B. Prescott	775
An Improved Gas Regulator. By F. P. Dunnington	781
Inspection of Cotton for Use in the Manufacture of Guncotton. By Charles E. Munroe	783
Reduction with Magnesium Amalgam. By Hermann Fleck and Lewis L. Bassett	789
Two Definite Carbides of Iron with Chromium (Molybdenum and Tungsten). By James S. de Benneville	791
On the Possibility of the Occurrence of Hydrogen and Methane in the Atmosphere. By Francis C. Phillips	801
A New Generator. By Edward P. Harris	809
The Determination of Tannin by Metallic Oxides. By William H. Krug	811
The Estimation of Sulphur in Refined Copper. By G. L. Heath	814
Acidimetric Estimation of Vegetable Alkaloids. By Lyman F. Kebler	822
NEW BOOKS: Elements of Modern Chemistry; Justus Von Liebig, His Life and Work	832
NOTE: Determination of Acetic Acid in Vinegar	834

## NOVEMBER.

An Electrolytic Process for the Manufacture of White Lead. By R. P. Williams	835
The Chlorides of Zirconium. By F. P. Venable	842
The Determination of the Heating Effects of Coals. By W. A. Noyes, J. R. McTaggart, and H. W. Craver	843
Tellurium: Its Separation from Copper Residues with Notes on Some New Reactions. By Cabell Whitehead	849

The Electrolytic Reduction of Paranitro Compounds in Sulphuric Acid Solution. By Arthur A. Noyes and John T. Dorrance.....	855
Periodides of Pyridine. By A. B. Prescott and P. F. Trowbridge....	859
On the Analysis of Alloys of Lead, Tin, Antimony and Arsenic. By Launcelot Andrews.....	869
The Determination of Graphite in Pig Iron. By P. W. Shimer.....	873
On the Composition of Pelagine. By A. B. Griffith and Charles Platt	877
On the Volumetric Determination of Titanic Acid and Iron in Ores. By H. L. Wells and W. L. Mitchell.....	878
Arsenic in Glycerol. By G. E. Barton.....	883
The Occurrence of Trimethylene Glycol as a By-Product in the Glycerol Manufacture. By Arthur A. Noyes and Willard H. Watkins .....	890
The Evolution Method for the Determination of Sulphur in White Cast-Iron. By Francis C. Phillips.....	891
On the Volumetric Determination of Lead. By Allerton S. Cushman and J. Hayes-Campbell.....	901
Reactions Between Copper and Concentrated Sulphuric Acid. By Chas. Baskerville .....	904
NEW BOOKS: Principles and Practice of Agricultural Analysis; A Hand-Book of Industrial Organic Chemistry.....	912
Books Received.....	916

## DECEMBER.

A Convenient Still for the Laboratory. By Charles E. Wait.....	917
On the Estimation of the Extraction in Sugar Houses. By M. Trubek.....	920
On Silicides of Iron. By G. de Chalmot.....	923
Estimation of Phosphoric Acid in Soils by Double Precipitation with Molybdic Solution and Titration of the Ammonium Phosphomolybdate with Standard Alkali. By C. B. Williams....	925
On the Use of Organic Bases in the Preparation of Barium and Calcium Ferrocyanides. By Percy H. Walker.....	927
On the Formation of Layers in Mixtures of Acetic Acid and Benzene. By C. E. Linebarger.....	932
Scheme for the Identification of Acetaldehyde, Phenacetine, Quinine Sulphate, etc. By F. S. Hyde.....	933
On the Physical and Chemical Properties of Some California Oils. By Walter C. Blasdale.....	935
The Determination of Phosphoric Acid by the Molybdate-Magnesia Method, and by Volumetric Method. By B. W. Kilgore .....	941
The Volumetric Estimation of Manganese. By George Auchy .....	943
An Early Arrangement of the Elements. By F. P. Venable.....	947
On the Estimation of Phosphoric Acid by Titration of the Ammonium Phosphomolybdate Precipitate with Standard Alkali. By B. W. Kilgore.....	950
The Relationship of the Heat of Vaporization of Gases to their Density and also to their Boiling Point. By Wm. L. Dudley.....	969
The Determination of Methane and Hydrogen by Explosion. By Augustus H. Gill and Samuel P. Hunt.....	986
NEW BOOKS: A Manual of Qualitative Chemical Analysis; Principles and Practice of Agricultural Analysis; Laboratory Work in Chemistry.....	994
Books received.....	997
NOTE: The Banquet to Messrs. Mond and Tyrer.....	997
Errata.....	999
A Tribute to Pasteur .....	1000

## Proceedings.

### NEW MEMBERS ELECTED NOV. 30, 1894.

Alexander, Heald H., care of Globe Smelting and Refining Company,  
Denver, Colo.

Donaldson, Sidney T., Frost Laboratory, 34 Broad St., Charleston, S. C.

Eddy, Harrison P., City Hall, Worcester, Mass.

Fuller, Fred. D., Durham, N. H.

Guteman, Franklin, Cooper Block, Denver, Colo.

How, Fred W., Durham, N. H.

Leighton, Virgil L., A.B., Lawrence, Kan.

McKeen, James, Tilly Foster, Putnam Co., N. Y.

Morse, Prof. Fred W., Durham, N. H.

Paruly, Dalton, Sharpville, Pa.

Proctor, Richard W., care of Wm. S. Merrell Chemical Company,  
Cincinnati, Ohio.

Schaeffer, Henri, Manchester Mills, Manchester, N. H.

Sherman, H. C., College Park, Md.

Stone, Edward P., Durham, N. H.

Tonceda, Enrique, Hoosick Falls, N. Y.

Traphagen, Dr. F. W., Bozeman, Mont.

Ullman, Dr. H. M., Lehigh University, South Bethlehem, Pa.

Veitch, F. P., College Park, Md.

---

### ELECTED DEC. 10, 1894.

Allen, W. M., Raleigh, N. C.

Clarke, Thomas, Chapel Hill, N. C.

Clymer, Edwin S., 1012 North 10th St., Reading, Pa.

Cooke, George T., 103 Milk St., Boston, Mass.

Field, Charles, 3rd, 2013 Green St., Philadelphia, Pa.

Glover, Henry, East Falls of Schuylkill, Philadelphia, Pa.

Harris, J. R., B.S., Johns Hopkins University, Baltimore, Md.

Irish, Cyrus W., Lowell High School, Lowell, Mass.

Mason, A. H., F.C.S., F.R.M.S., care of Seabury and Johnson, 59 and 61 Maiden Lane, New York City.

Miles, George W., Jr., 103 Milk St., Boston, Mass.

Peter, Alfred M., 171 Rose St., Lexington, Ky.

Prentiss, George N., 226 Grand Avenue, Milwaukee, Wis.

Sanders, C. N., Pulaski City, Pulaski Co., Va.

Scovell, M. A., Lexington, Ky.

Seldner, Rudolph, 217 Jefferson Avenue, Brooklyn, N. Y.

Siegfried, Alfred A., 39 South St., Jersey City, N. J.

Smolt, Frank O., Aspen, Colo.

Waite, Charles N., Rumford Falls, Me.

#### CHANGES OF ADDRESS.

Brown, W. G., Division of Chemistry, Department of Agriculture, Washington, D. C.

Forbes, Fred B., Experiment Station, Lawrence, Mass.

Hewitt, Edward R., Room 8, East 9th St., New York City.

Mumper, W. N., 228 West State St., Trenton, N. J.

Waterman, C. N., 345 Decatur St., Brooklyn, N. Y.

Weems, J. B., Experiment Station, Geneva, N. Y.

---

### MEETINGS OF THE SECTIONS.

---

#### NEW YORK SECTION.

Friday Evening, Dec. 14, 1894.

Prof. P. T. Austen, presiding.

Forty members present.

Dr. Thomas B. Osborne, of New Haven, read a paper on the Chemical Nature of Diastase, showing that by successive treatment with ammonium sulphate, solution in water, dialysis into alcohol, and extraction with sodium chloride solution, a nitrogenous substance can be prepared from malt extract which has an enormous diastatic power, and that by this means pure diastase may be isolated.

Dr. Bartley presented facts to prove the injurious effects of

(3)

glucose upon the digestion, and commented upon the probable reasons therefor.

Prof. Austen presented an essay upon careless diction in chemical text-books.

#### WASHINGTON SECTION.

Nov. 8, 1894.

President W. H. Seaman in the chair.

Ten members present.

The resignation of Prof. J. C. Gorden was read and accepted.

A letter from John W. Hoyt was read, asking the co-operation of the Society in the formation of a National Post-Graduate University. The President of the Society was asked to assure Mr. Hoyt of the sympathy and co-operation of the Society.

H. W. Wiley reported as to the First Congress of Chemists at the San Francisco Exposition, and referred to the probable formation of a Local Section of the American Chemical Society on the Pacific Coast.

A paper was read by W. D. Bigelow on the "Coloring Matter in California Red Wines." This was a preliminary notice of work, not yet completed, which will later be made the subject of a more extended communication. He had subjected samples of ninety-four varieties of California red wines to the same examination as that commonly applied for the coloring matter in European wines. "According to the reactions obtained with these reagents, the coloring matter of California wines appears to be much more uniform than that of European wines. Sometimes, however, a gray, or yellowish, or orange-gray precipitate or solution is obtained with reagents which are said to give a green or grayish-green with French wines. On the other hand, no reactions were obtained which are said to be characteristic of wines colored with vegetable pigments."

#### *Discussion.*

Dr. Wiley said that the inducements for adulteration of California wines were not great on account of their low price. The difficulties in distinguishing between a natural and a spurious

(4)

article became very great at a point where the results of analyses might just as readily be interpreted one way as another, and to obtain greater certainty beyond this point the work was undertaken in the laboratory of the Agricultural Department.

Mr. Bigelow, in response to the question as to the success of the use of the spectroscope in the examination of wines, said that it had been employed with some success in the detection of cochineal and of the coal-tar colors, but for the detection of vegetable colors it was unsatisfactory, owing to the fact, no doubt, that they were so closely allied to the natural colors of the wine.

## Proceedings.

### ANNUAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The tenth general meeting of the American Chemical Society was held in Boston and Cambridge, Mass., Dec. 27th and 28th, 1894.

The Society was called to order at 10.20 A. M., Thursday, Dec. 27th, at the Massachusetts Institute of Technology, in room No. 22, of the Walker building.

Dr. T. M. Drown made a brief address of welcome to which President Wiley responded on behalf of the Society. Dr. Wiley expressed the special pleasure which the visiting chemists felt in meeting in the Massachusetts Institute of Technology, an Institution which has done so much for the advancement of science.

Mr. C. Tennant Lee, chairman of the Local Committee of Arrangements, made some announcements, and stated that on account of the inclement weather it would hardly be expedient to carry out the program which had been arranged for visits to the Experiment Station of the State Board of Health, and the Rubber Shoe Manufactory at Malden during the afternoon.

The minutes of the last general meeting were read and approved, and the minutes of the former meetings were also approved, as recorded by the General Secretary.

The General Secretary then read his annual report, which was as follows:

TO THE MEMBERS OF THE AMERICAN CHEMICAL SOCIETY:

GENTLEMEN: In presenting my annual report at the close of the present administration, a brief retrospective view of the organization and development of the Society, and a glance at its present condition will enable the members to gain instruction and encouragement from the past, hope and inspiration from the present, and a bright and confident outlook upon the future.

The American Chemical Society was the outgrowth of a

meeting of American chemists held in Northumberland, Pa., in August, 1874, to celebrate the centennial of the discovery of oxygen by Priestley. The Society was organized in 1876 and incorporated October 25, 1877. Its inception was vigorous, and those who took part in its organization had high hopes for the position it would occupy among the scientific societies of the world, for the inspiration and aid it would afford those who were engaged in chemical pursuits or in preparing others for such vocations, and for the ever increasing stimulus it would furnish to chemical science and industry throughout the American continent.

From the beginning the Society published regularly a Journal of its proceedings, including papers and discussions; many of the leading chemists of the country were enrolled in its membership; quite a number of prominent chemical manufacturers were among its associates; and the names of foreign chemists of distinction were upon its roll, either as active or as honorary members.

The following is a list of persons who have served the Society as its President:

*1876, J. W. Draper.	1886, A. B. Prescott.
*1877, J. Lawrence Smith.	1887, C. A. Goessmann.
1878, S. W. Johnson.	*1888, T. Sterry Hunt.
*1879, T. Sterry Hunt.	1889, C. F. Chandler.
*1880, F. A. Genth.	1890, H. B. Nason.
1881, C. F. Chandler.	1891, G. F. Barker.
1882, J. W. Mallet.	1892, G. C. Caldwell.
*1883, J. C. Booth.	1893, H. W. Wiley.
*1884, J. C. Booth.	1894, H. W. Wiley.
*1885, J. C. Booth.	

It is not until within the past few years, however, that the Society has fully justified the hopes of its founders that it would be in all respects a representative national organization. Its membership extended throughout the entire country and even included persons of other countries upon our own continent and in Europe, but, inasmuch as the meetings were all held in New York City, the members in other localities did not come into so active relation with the Society and its work as was desirable, and could not be prevailed upon to take sufficient interest in its

\* Deceased.



welfare, nor to assume their share of responsibility in its management. Under these conditions there gradually developed among the members in other parts of the country the erroneous impression that the Society was local rather than national in its efforts and aims, and this impression was deepened by the fact that a number of prominent chemists throughout the country had either never been members of the Society or had withdrawn from active connection with it.

This state of affairs was unsatisfactory to every one, and it devolved heavy burdens upon the members residing in New York City and vicinity. There was no alternative, however; those members were obliged to carry the burden with heroic self-sacrifice until some plan could be devised by which the interest and active co-operation of a large body of chemists throughout the country could be permanently enlisted. To this end they labored with persistent determination and with unshaken faith in the ultimate result. The American Chemical Society had been recognized abroad for years as the organized body of the chemists of North America; it had already acquired something of prestige and established rights; and those who were made responsible for its management believed that it could be made to command the active support of the chemists of this continent, and to secure for them and their work adequate recognition among the chemists of the world.

The conferences, struggles, concessions, appeals to American chemists everywhere, whether members of the Society or not, and the hearty response to those appeals which was received from all over the country, need not be recounted here; but they will ever remain a noble example of self-sacrifice and true devotion to the welfare and progress of chemical science upon this continent.

The plan finally adopted by the chemists who had part in these counsels and efforts was to utilize what the American Chemical Society had already gained, to broaden and strengthen its foundation, and to effect radical changes in its management and operations. These changes were so outlined and provided for by the Society as to induce large numbers of prominent chemists, who had hitherto held aloof, to become members of the

Society and to add their influence, their energies, and their counsel to the forces that were already in operation to secure a complete and satisfactory reorganization of the Society.

Among the most effective measures adopted and continued up to the present time are the following :

(1) The management of all the important affairs of the Society is entrusted to a council of fifteen, composed of twelve members regularly chosen by ballot at the annual election of the Society—four elected each year, to serve for a period of three years—and in addition, the President, the General Secretary, and the Editor, ex-officio. The members of the council for the year 1894 are :

H. W. Wiley, Washington, D. C., President.  
 Albert C. Hale, Brooklyn, N. Y., General Secretary.  
 Edward Hart, Easton, Pa., Editor.  
 J. H. Appleton, Providence, R. I.  
 G. F. Barker, Philadelphia, Pa.  
 G. C. Caldwell, Ithaca, N. Y.  
 F. W. Clarke, Washington, D. C.  
 C. B. Dudley, Altoona, Pa.  
 W. L. Dudley, Nashville, Tenn.  
 J. W. Mallet, Charlottesville, Va.  
 Wm. McMurtrie, New York, N. Y.  
 T. H. Norton, Cincinnati, O.  
 A. B. Prescott, Ann Arbor, Mich.  
 Alfred Springer, Cincinnati, O.

(2) Local sections are established in different parts of the country, after the plan of the British Society of Chemical Industry. The presiding officers of the sections constitute the vice-presidents of the Society. Six local sections exist now, and there is a good prospect for the early formation of two or three more. Those already chartered are :

Rhode Island Section : Presiding Officer, Charles A. Catlin, 133 Hope St., Providence, R. I. ; Secretary, E. E. Calder, Board of Trade Building, Providence, R. I.

Cincinnati Section : Presiding Officer, J. U. Lloyd, Court and Plum Sts., Cincinnati, O. ; Secretary, E. C. Wallace, Room 71, Blymeyer Building, Cincinnati, O.

New York Section : Presiding Officer, Peter T. Austen, Polytechnic Institute, Brooklyn, N. Y. ; Secretary, Morris Loeb, 37 East Thirty-eighth St., N. Y. City.

Washington Section : Presiding Officer, W. H. Seaman, 1424 Eleventh St., Washington, D. C.; Secretary, A. C. Peale, 605 Twelfth St., Washington, D. C.

Lehigh Valley Section : Presiding Officer, W. H. Chandler, South Bethlehem, Pa.; Secretary, Albert H. Welles, Lafayette College, Easton, Pa.

New Orleans Section : Presiding Officer, A. L. Metz, Tulane Medical College, New Orleans, La.; Secretary, Hubert Edson, Bartels, La.

(3) Two general meetings of the Society are held each year, the time and place of these meetings being determined by the council. General meetings have been held as follows:

1. Newport, R. I., August 6 and 7, 1890.
2. Philadelphia, Pa., December 30 and 31, 1890.
3. Washington, D. C., August 17 and 18, 1891.
4. New York, N. Y., December 29 and 30, 1891.
5. Rochester, N. Y., August 16 and 17, 1892.
6. Pittsburg, Pa., December 28 and 29, 1892.
7. Chicago, Ill., August 21 and 22, 1893.
8. Baltimore, Md., December 27 and 28, 1893.
9. Brooklyn, N. Y., August 15 and 16, 1894.

The change in membership during the past few years, since it was decided to arrange for general meetings of the Society to be held semi-annually in different localities, may be seen from the following statistics taken from the list of members published each year :

Nov. 1889,	169	members,	28	associates,	8	honorary members,
Nov. 1890,	203	"	27	"	8	"
Nov. 1891,	269	"	24	"	9	"
Nov. 1892,	319	"	25	"	7	"
Sept. 1893,	423	"	30	"	7	"
Sept. 1894,	664	"	50	"	8	"
Dec. 1, 1894,	700	"	55	"	8	"
" 26, 1894,	720	"	55	"	8	"
Total, 783.						

The present status as to membership should be given as follows :

Official roll of members.....	783
Elected but not required to qualify before Jan. 1,	
1895 .....	37
Applications now pending, no doubt of election...	30
Total.....	850

By inspection of the foregoing figures it will be seen that the membership of the Society has more than doubled during the past two years, and has more than quadrupled since November, 1889.

(4) The Journal of the Society appears on the first of each month throughout the year, each number containing at least seventy-two pages, making a yearly volume of the minimum size of 864 pages. It has been found necessary, however, to enlarge the size of some of the numbers, and that for December, 1894, includes about 100 pages of papers and discussions in addition to proceedings, etc. It is the intention of the Society to make this the leading and representative chemical journal of the United States, and one of the most important scientific periodicals to be found anywhere. It will contain the papers read before the various sections of the Society and before its general meetings, together with such abstracts relating to the progress of chemical science and industry as may be necessary. A prominent feature will be its effort to represent industrial and commercial chemistry. Each branch of chemical science will receive due attention and support, and those engaged in any kind of chemical research, or in the application of chemistry to the arts, will find in the JOURNAL a wide scope for publication. Through this medium the followers of each branch of chemistry will be brought into intimate contact with each other, and will know also what those in other branches of chemistry are doing, and what progress is making in all directions.

During the year 1894, by order of the council, the General Secretary has been charged with the duty of collecting all the membership dues. A large amount of arrears has been collected, and we believe that the percentage of arrears at present is lower than ever before. The financial report of the General Secretary is presented in a separate statement.

At the beginning of the year, Edward Hart was reappointed editor, and the regular standing committees for the year were selected.

A committee, consisting of F. W. Clarke, Chairman, Albert C. Hale, Secretary, and W. L. Dudley, was appointed by the President, on authority of the council, to receive and consider

suggestions for amending the constitution, the main object sought being to have only one governing body for the Society, instead of two—the Council and the Board of Directors—as at present; this body to be selected from the membership without regard to the locality of their residence.

By the action of the Board of Directors the General Secretary was instructed to place on file a certificate of incorporation of the Society, signed by all of the directors, and so worded that the majority of the Board of Directors shall not be required to be residents of the State of New York. Upon presenting such certificate at the office of the Secretary of State in Albany, N. Y., it was rejected on the ground that, under the laws now existing such an amendment can not be made. Upon this, the Board of Directors, with the recommendation of legal counsel, took the following action: "*Resolved*, That the Board of Directors hereby request the American Chemical Society, at its annual meeting, to authorize the taking of such steps as may be necessary to secure the passage of a bill by the Legislature of the State of New York, which shall so change the present laws of the State as to allow the Society to choose its directors without regard to their being residents of the State of New York, or of any other State or locality."

At the summer meeting of the Society, held in Brooklyn, N. Y., August 15 and 16, 1894, Dr. Wolcott Gibbs, of Newport, R. I., was unanimously elected an honorary member of the Society. This is the first time an American has been elected to honorary membership. Upon being informed by telegraph of this action, Dr. Gibbs sent a reply expressing his sincere thanks to the Society, and his high appreciation of the honor they had conferred upon him. An engrossed certificate of his election, signed by every member of the council, has been forwarded to Dr. Gibbs in accordance with the provisions of the constitution.

During the year, charters have been granted by the Board of Directors for the formation of two new local sections, on Feb. 15, for the Lehigh Valley Section, and August 15, for the New Orleans Section. The charters for both of these have been forwarded and the Sections have been organized.

The outlook has never before been so promising as it is to-day.

The Society is now founded upon a broad and strong basis, and its mode of organization allows a ready modification of its management whenever experience may indicate that changes are desirable. The plan of holding general meetings twice a year, in different localities, strengthens the Society, rapidly extends its influence, and brings the chemists of the country into personal acquaintance with one another and into a knowledge of the vast amount of successful work which is done by them upon this continent. The formation of local sections deepens the interest felt in the general Society, and stimulates scientific activity and enterprise in those localities where such sections are established. The growth of the Society in numbers and influence has been almost phenomenal within the past few years, and when we consider its present attainments, and the number and standing of those who are now upon its roll of membership we may confidently assert that the American Chemical Society to-day takes rank with the leading organizations of its kind in the civilized world.

Respectfully submitted,

ALBERT C. HALE,

General Secretary.

BROOKLYN, N. Y., December 26, 1894.

## FINANCIAL REPORT OF GENERAL SECRETARY OF AMERICAN CHEMICAL SOCIETY.

DECEMBER 1, 1894.

Dues collected for the year 1892 .....	\$	15.00	
" " " " 1893 .....		193.00	
" " " " 1894 .....		2,851.00	
" " " " 1895 .....		105.00	
Interest received on bank deposit.....	5.73	\$3,169.73	
Commissions deducted, 10% on \$3,162.50.....		316.25	
Remitted to Treasurer.....	\$2,655.00		
Balance in bank, December 1, 1894.....	198.48	2,853.48	
Total receipts .....		\$3,169.73	
Commissions deducted, 10% on \$3,162.50.....		316.25	
Amount due Treasurer:			
Account rebate to Local Sections .....	\$30.33		
Commission overdraft F. W. Traphagen.....	.15	30.48	

Commission due General Secretary from dues received by Treasurer on General Secretary's account, 10% on \$20.00.....	2.00
Balance due Treasurer from General Secretary...	28.48
Net commission of General Secretary .....	\$287.77

After this the Treasurer's report was read by the Secretary and adopted, it having been previously audited by the Finance Committee.

## AMERICAN CHEMICAL SOCIETY.

### TREASURER'S REPORT FOR 1894.

#### *Receipts.*

Balance on hand, December 22, 1893.....	\$ 74.05
Dues collected by Treasurer.....	622.09
Net dues and interest received from Secretary.....	2,853.48
Net commissions returned by Secretary .....	28.48
Cash received for subscriptions to Journal.....	575.42
"    "    " back numbers .....	159.48
"    "    " advertisements in Journal.....	131.80
"    "    " cancelled insurance policy .....	31.64
"    "    " Furniture sold to University C. N. Y.....	100.00
	<u>\$4,576.44</u>

#### *Disbursements.*

Expense of Journal and editorial office .....	\$2,890.27
"    " Secretary's office .....	413.12
"    " Treasurer's office.....	24.72
"    " Librarian's office .....	153.50
"    " Baltimore meeting (balance) .....	4.50
"    " Brooklyn meeting.....	60.55
General expense.....	16.50
Insurance.....	84.00
Rebate paid to Treasurer of N. Y. Local Section .....	200.00
"    "    "    " Washington Section....	101.67
"    "    "    " Rhode Island Section.....	28.33
"    "    "    " Cincinnati Section.....	63.33
"    "    "    " Lehigh Valley Section .....	30.00
Balance on hand Dec. 22, 1894, in Bank of Metropolis, \$505.19	
Postage stamps.....	.76
	<u>\$4,576.44</u>

CHAS. F. MCKENNA, *Treasurer.*

No bills or claims, presented up to date and audited, remain unpaid.  
Accounts examined and found correct, E. and O. E.

A. P. HALLOCK,  
DURAND WOODMAN,  
FRANK T. KING,

New York, Dec. 22, 1894.

*Finance Committee.*

Professor Edward Hart, Editor of the Society's publications, gave an oral report showing what had been done in connection with the publication of the Journal of the Society, and explained how the scope of the Journal could be widened and that periodical maintained at the highest standard of excellence.

The report of the Librarian was then called for, but as the Librarian was absent and no report had been sent in, Professors A. H. Sabin, of Long Island City, and Wm. McMurtrie, of New York, presented informal statements of the condition of the library. Upon the request of the President, the report of the Librarian was ordered to be spread upon the minutes when it should be received by the Secretary.

The Society then proceeded to the order of general business, and, upon the motion of Professor A. C. Hale, adopted the following:

*Resolved*, That the General Secretary of the American Chemical Society is hereby authorized and requested, to take such steps as may be necessary to secure the passage of a bill by the Legislature of the State of New York, which shall so change the statutes of said State as to allow the Society to choose its Directors without regard to their being residents of the State of New York, or of any other state or locality.

The arranged program was then taken up, and a paper entitled "Note on the Estimation of Iron and Alumina in Phosphates," by K. P. McElroy, was read by the General Secretary. Dr. Thos. M. Drown then followed with a description of the Lawrence Experiment Station of the Massachusetts State Board of Health, and the nature of the work which was carried on there for the purification of the sewage and water. He distributed among the chemists present, copies of two tables showing methods and results of the experiments of the Station. Dr. Drown mentioned four methods of filtration in use, that had been tried at the Experiment Station; namely, rapid filtration through gravel, aided by a current of air, chemical precipitation, sedimentation, and straining through coke. The result obtained through the first system was particularly valuable; no other method had been found so capable of rapidly purifying a large amount of sewage. By means of this method some six or seven hundred thousand gallons were purified daily, and the effluent



rendered as wholesome as ordinary spring water. Dr. Drown then spoke of the results which had followed the purification of the drinking water and pronounced them marvelous. In Lowell and Lawrence the death-rate from typhoid fever had been three times greater than the normal. The inhabitants were mostly operators in mills and obtained their drinking water from the Merrimac river, which was contaminated by the sewage of the cities and towns along its course; since the purification of the water by rapid filtration through gravel, the death-rate and number of cases from typhoid fever had been diminished to an unprecedented degree. The money for these experiments had been appropriated by the State of Massachusetts, and the result justified the confidence placed in the State Board of Health and its experiments. After some questions and discussions upon Dr. Drown's remarks, a paper entitled, "The Coloring Matter in California Red Wines," was read by W. D. Bigelow.

Two papers were read by title; namely, "An Examination of the Atmosphere of Cleveland, Ohio," by C. F. Mabery, and "Rainfall and Typhoid Fever," by Wm. P. Mason, Troy, N. Y.

Mr. J. O. Handy then read a paper on "The Advantages in the Use of Barium Hydrate Solution as an Absorbent in Carbon Determination in Steel."

After this Professor C. E. Munroe read a paper by J. E. Blomen, on "Some Practical Points on the Manufacture of Nitro-Glycerine," and a paper by himself upon "Tellurium from Copper Residues," and exhibited an ingot of tellurium prepared in the laboratory of the Columbian University, which is believed to be the largest specimen of that metal ever obtained. The ingot was about six inches in length, one and one-half inches in width, and something more than one-fourth of an inch in thickness, showing beautiful metallic luster and crystalline formation; it weighed 16.7 ounces; at the quoted price of this element the value of the ingot would be something over \$250.

Professor Munroe then presented a paper, by Cabell Whitehead, on "The Estimation of Tellurium in Copper Bullion, and Professor Edward Hart read a paper entitled "Some Points in the Distillation of Nitric Acid." After some announcements, the Session adjourned at 1 P. M.

Upon the adjournment of the Session the chemists went directly to the Union Station, at Causeway St., where lunch was served by the Local Committee.

The weather having become fairly pleasant, it was decided here to take the train for Malden, after lunch, and visit the manufactory of the Boston Rubber Shoe Company, at Fells Station. Arriving at this destination, the chemists were very cordially received by the Superintendent, Mr. Robson, who escorted the party to the various departments in the building, carefully explaining to them all details of the various processes. They were shown first the washroom, where crude rubber from Para, Central America, and Africa, was sheeted and cleaned by running through the heavy rollers with a current of water pouring down upon it; next they were taken to the drying lofts, where the sheeted rubber is left for a few days exposed to the air at a temperature of 80°-90° F.; from this place the rubber is taken to the mixing room, where it is again run through heavy rollers, each having a different rate of speed; a mixture of vulcanizing agents (sulphur and litharge), coloring matter (lamp-black), inert filling (whiting), and reclaimed rubber and coal tar is then thrown upon the sheeted rubber as it passes between the rollers, which by their different rates of speed produce an effect like the kneading of dough, so that the material is thoroughly intermixed with the rubber, forming a homogeneous mass. The stock thus prepared is soft and extremely adhesive, its surfaces uniting firmly and permanently by contact and pressure. For convenience in handling, its adhesiveness can be temporarily removed by dusting the surfaces with flour, talc, etc.

The sheets formed by passing this material between the rollers can be prevented from sticking together by interposing plain sheeting for wrapping cloth, and they are transferred to the cutting room on cloth frames. All of the cutting is done on wooden blocks or zinc surfaces; the different methods of cutting are: *a.* Hand-knife and metal template. *b.* Hand die and mallet. *c.* Machine die. *d.* Machine knife (soles only). Fabrics are cut several thicknesses at once; sheet rubber singly.

Engraved surfaces, such as uppers and soles for rubber shoes, are made by passing the sheet rubber between rollers having

corresponding figures. Throughout all the processes of manufacture, except the making of heels, the rubber remains unvulcanized until everything else is done, vulcanization being the last step of all. Heels for heavy overshoes are made by hydraulic steam-jacketed presses, which form and vulcanize them at the same time.

In the boot and shoe rooms proper, the operations are as follows: *a.* Lasting innersole and lining over maple last. *b.* Applying the stay pieces, straps, etc. *c.* Covering outside with cloth or rubber upper. *d.* Attaching the soles. Each part requires to be rolled in place to insure adhesion and perfect contact. All dry surfaces are brushed over with rubber cement (solution of rubber compound in naphtha). Such goods as are to have a bright finish receive a coat of thin linseed-oil varnish previous to vulcanization.

The completed goods containing the lasts are vulcanized on iron cars, in chambers heated by steam coils. Temperature, 260°–270° F. Time, six to seven hours. The temperature is equalized and the volatile products removed by ventilation.

After vulcanization the lasts are removed and the boots and shoes packed for shipment.

#### SECOND DAY'S SESSION.

The meeting was called to order at 10.15 A. M. in the Chemical Lecture Room, Boylston Hall, Harvard University, Cambridge, Mass.

Professor C. Loring Jackson welcomed the chemists to Cambridge and the University; he described the location and arrangement of the various laboratories, museums, etc., which would be open for inspection after the morning session. President Wiley made some very appropriate remarks in response, after which the following papers were read:

Methods for the Examination of Glycerine for use in the Nitro-Glycerine Manufacture, by G. E. Barton. Read by title.

Report of the Committee on Atomic Weights for 1894, by F. W. Clarke. Read by the Secretary.

The Volumetric Determination of Phosphorus in Steel, by W. A. Noyes and J. S. Royse. Read by C. B. Dudley.

Note on the Manufacture of Zein, by A. H. Sabin.

The Volumetric Determination of Orcin, by H. S. Neiman.  
Read by title.

Note on the Purification of Glucinum Salts, by Edward Hart.

The Estimation of Sulphur in Pyrites, by George Lunge.  
Read by Edward Hart.

Some New Forms of Extractive Apparatus, by A. E. Knorr.  
Read by title.

Recent Work on the Atomic Weight of Oxygen, by E. W. Morley.

After Professor Morley's paper the Committee of Canvassers made their report, and the President announced the result of the annual election, which was as follows:

*President*—Edgar F. Smith, Philadelphia.

*General Secretary*—Albert C. Hale, Brooklyn.

*Treasurer*—C. F. McKenna, New York.

*Librarian*—F. E. Dodge, Brooklyn.

*Directors* (to serve two years)—H. W. Wiley, Washington; Wm. McMurtrie, New York; J. H. Appleton, Providence; A. A. Breneman, New York.

*Councilors*—(to serve three years)—F. W. Clarke, Washington; W. L. Dudley, Nashville; E. R. Squibb, Brooklyn; G. F. Barker, Philadelphia.

Upon the motion of Edward Hart, the Society unanimously passed a vote of thanks to the following individuals and corporations for courtesies received: Corporation and Faculty of the Massachusetts Institute of Technology; also Corporation of Harvard University; Dr. Thos. M. Drown; Professor C. Loring Jackson; Professor H. B. Hill; to the Boston Rubber Shoe Co., and Superintendent Robson; Authorities of the State Experiment Station at Lawrence, Mass., and members of the Associated Press. The address of the retiring President, "The Synthetic Food of the Future," was then presented by H. W. Wiley. At the close of the address, Dr. Wiley reviewed the history of the Society during the two years of his presidency, and expressed his thanks to the members, and especially to the various officers of the Society, who had aided him in making such marked advancement in numbers, in the character of the work and publications, and in the general reputation which the Society had gained throughout the world.

The Society then adjourned its session, and the chemists were tendered a lunch at the Colonial Club. The remainder of the

day was spent in examining the various laboratories, museums, and collections of the University.

The following named persons were registered in attendance at the meeting:

H. W. Wiley, Washington, D. C.  
Edward Hart, Easton, Pa.  
Albert C. Hale, Brooklyn, N. Y.  
Charles L. Parsons, Durham, N. H.  
Chas. W. Moulton, Poughkeepsie, N. Y.  
C. H. White, Naval Laboratory, Brooklyn, N. Y.  
T. M. Drown, Mass. Inst. Téch., Boston, Mass.  
Chas. B. Dudley, Altoona, Pa.  
Wm. McMurtrie, 106 Wall St., New York City.  
Ellen H. Richards, Boston, Mass.  
Arthur A. Noyes, Boston, Mass.  
Augustus H. Gill, Mass. Inst. of Tech., Boston, Mass.  
Walter S. Allen, Boston Gas Light Co., Boston, Mass.  
William K. Robbins, Manchester, N. H.  
Charlotte A. Bragg, Wellesley, Mass.  
Mary E. Mathews, Painesville, Ohio.  
Henry P. Talbot, Mass. Inst. Tech., Boston, Mass.  
Walter L. Jennings, Boston, Mass.  
Thomas Evans, Mass. Inst. Tech., Boston, Mass.  
S. Lawrence Bigelow, Boston, Mass.  
William T. Hall, 222 Marlborough St., Boston, Mass.  
Rolfe M. Ellis, Hyde Park, Mass.  
Chas. H. Miller, Baltimore, Md.  
Chas. T. Pomeroy, Newark, N. J.  
Durand Woodman, New York City.  
Walter M. Saunders, Olneyville, R. I.  
H. J. Wheeler, Kingston, R. I.  
W. D. Bigelow, Washington, D. C.  
Walter E. Smith, Providence, R. I.  
Jas. O. Handy, Pittsburg, Pa.  
Herbert L. Lamborn, Alliance, Ohio.  
Henry H. Tozier, Haverhill, Mass.  
Chas. W. Hapgood, Everett, Mass.  
E. H. Laws, Bedford, Mass.  
Sidney S. Emery, Philadelphia, Pa.  
David B. Weston, Sharon, Mass.  
Charles A. Meserve, Allston, Boston, Mass.  
Albert Dunbar, Pittsfield, Mass.  
C. Tennant Lee, Boston, Mass.  
Bennett F. Davenport, Boston, Mass.

Edward W. Morley, Cleveland, Ohio.  
 Charles E. Munroe, Washington, D. C.  
 J. M. Crafts, Inst. of Technology, Boston, Mass.  
 J. H. Long, Chicago, Ill.  
 Severance Burrage, Inst. of Technology, Boston, Mass.  
 Frederick W. Howe, Durham, N. H.  
 Lewis H. Kittredge, Durham, N. H.  
 Charles A. Pitkin, South Braintree, Mass.  
 Charles A. Catlin, Providence, R. I.  
 George F. Andrews, Providence, R. I.  
 John H. Washburn, Kingston, R. I.  
 J. F. McGregory, Hamilton, N. Y.  
 J. W. Ellins, Framingham, Mass.  
 S. P. Sharples, Boston, Mass.  
 Walter Woodman, M.D., Cambridge, Mass.  
 A. H. Sabin, Long Island City, N. Y.  
 Albert M. Todd, Kalamazoo, Mich.  
 W. P. Cutter, Washington, D. C.  
 Howard C. Saunders, Providence, R. I.  
 Leonard P. Kinnicutt, Worcester, Mass.  
 Edw. P. Harris, Chester, Pa.  
 John B. Stearns, University of Vermont.  
 W. R. Orndorff, Ithaca, N. Y.  
 R. P. Williams, Boston, Mass.  
 Thomas B. Osborne, New Haven, Conn.  
 W. R. Livermore, Boston, Mass.  
 John F. Bannan, North Andover, Mass.  
 Horace A. Bishop, Providence, R. I.  
 Fred. L. Thayer, Providence, R. I.  
 Frank N. Smalley, Westboro, Mass.  
 S. D. Gage, Mass. Inst. Tech., Boston, Mass.  
 Harris E. Sawyer, Cambridge, Mass.  
 George Oenslager, Harrisburg, Pa.  
 Martin H. Ittner, St. Louis, Mo.  
 Frederick L. Dunlap, Chillicothe, Ohio.  
 Delia M. Stickney, Cambridge, Mass.  
 C. Belle Kenney, East Boston, Mass.  
 G. C. Hodges, Utica, N. Y.  
 A. E. Dolbear, Tufts College, Mass.  
 C. L. Jackson, Cambridge, Mass.  
 H. B. Hill, Cambridge, Mass.  
 Fred. W. Morse, Durham, N. H.  
 W. B. Lindsay, Dickinson College, Carlisle, Pa.  
 Stephen Freeman, Boston, Mass.

**COUNCIL.**

The bill for printing the December number of the JOURNAL, amounting to more than \$250, it was submitted to the Council according to the Constitution, and approved by them January 5, 1895.

**NEW MEMBERS ELECTED DECEMBER 26.**

Becher, Jesse B., Lincoln, Neb.  
 Brown, Lucius P., Nashville, Tenn.  
 Chase, Geo. W., Phillipsburg, N. J.  
 Franklin, Edward Curtis, Lawrence, Kan.  
 Grindly, Dr. H. S., East Green St., Champaign, Ill.  
 Harrison, Herbert E., B.S., Agricultural College, Mich.  
 Hiltner, Robert S., Lincoln, Neb.  
 Meeker, G. H., Longdale, Va.  
 Miller, Hugh L., Wilmington, N. C.  
 Nelson, E. K., 6814 Union Ave., Englewood, Ill.  
 Nicholson, Edward E., Lincoln, Neb.  
 Rossman, William L., B.S., Agricultural College, Mich.  
 Wardman, Geo. B., care of Detroit Copper Company, Morenci, Ariz.  
 White, A. H., West University Ave., Champaign, Ill.  
 White, John, Ph.D., Lincoln, Neb.

**ELECTED JANUARY 12.**

Barrows, W. A., Jr., Sharpville, Pa.  
 Beeson, J. L., care Audubon School of Sugar, Audubon Park, New Orleans, La.  
 Billings, Edgar F., 165 High St., Boston, Mass.  
 Fassett, Chas. M., Spokane, Wash.  
 Frohman, Edward D., 68 W. Third St., Cincinnati, Ohio.  
 Graham, Robert O., Bloomington, Ill.  
 Guess, George A., M.A., Fairview via. Penticton, B. C.  
 Homburg, Fred., 40 Clifton Ave., Cincinnati, Ohio.  
 Loewenstein, Harry, 144 Hackberry St., Cincinnati, Ohio.  
 Mather, Henry A., 27 Pierrepont St., Brooklyn, N. Y.  
 Neher, Fred., Princeton, N. J.  
 Peyton, William C., care The Cal. Powder Works, Santa Cruz, Cal.  
 Roth David M., 36 Ingleside Place, Cincinnati, Ohio.  
 Shaw, Professor G. W., Corvallis, Benton Co., Oregon.  
 Smith, J. D. Audley, Clifton, Ariz.  
 Swenson, M., Monadnock Block, Chicago, Ill.  
 Thorburn, A. D., 465 State St., Chicago, Ill.  
 Tucker, Francis F., Nebraska City, Neb.  
 Wrampelmeier, Theodore J., Custom House, San Francisco Cal.

ELECTED JANUARY 17.

Freeman, Stephen, 79 Montgomery St., Boston, Mass.  
Guild, Frank N., Greenboro, Vt.  
Johnson, Emil F., 96-98 Maiden Lane, N. Y. City.  
Miller, Edmund H., Ph.D., 41 East 49th St., N. Y. City.  
Newell, H. E., Saxtons River, Vt.  
Pickert, Lee W., Amer. Sugar Ref. Co., Granite St., South  
Boston, Mass.  
Redding, Allen C., Findlay, Ohio.  
Spaulding Edward G., 43 W. 32nd St., N. Y. City.  
Worcester, Charles P., State House, Boston, Mass.

ASSOCIATE ELECTED JANUARY 17.

Fosdick, Eugene H., San Diego, Cal. .

CHANGES OF ADDRESS.

Barton, G. E., Hatfield, Mass.  
Catlin, Chas. A., 133 Hope St., Providence, R. I.  
Clarke, F. W., U. S. Geological Survey, Washington, D. C.  
Dickerson, E. N., 253 Broadway, N. Y. City.  
Dudley, Chas. B., Drawer 334, Altoona, Pa.  
Eichberg, Julius H., M.D., 50 West 9th St., Cincinnati, Ohio.  
Hahn, A. G. C., care of Nepera Chemical Company, Nepera  
Park, N. Y.  
Jackson, C. E., care of Wm. S. Merrell Chemical Company,  
Cincinnati, Ohio.  
Kedzie, Frank S., 414 Ottawa St., Lansing, Mich.  
Lanning, John G., care of Cleveland R. M. Company, Cleve-  
land, Ohio.  
Latham, Woodville, Hotel Bartholdi, Madison Square, N. Y.  
City.  
Randolph, R. B. F., Hoagland Laboratory, Brooklyn, N. Y.  
Smith, Herbert E., Yale Medical School, New Haven, Conn.  
Wardman, Geo. B., care of John L. Elliot, Ahualulco, Estado  
de Jalisco, Mexico.

ADDRESSES WANTED.

Davis, G. C., old address, 311 W. Mahantonga St., Potts-  
ville, Pa.  
Ray, Victor, old address, Anaconda Electrolytic Refinery,  
Anaconda, Montana.



## MEETINGS OF THE SECTIONS.

---

### WASHINGTON SECTION.

Thursday, December 13, 1894.

The Society was called to order at 8 P. M. by the President, Dr. Seaman, with twenty members present. The minutes of the 76th meeting were read and approved.

The first paper of the evening was read by Mr. Carr on "The Dehydration of Viscous Organic Liquids," by Oma Carr and F. T. Sanborn.

The authors reviewed briefly the various accepted methods for the dehydration of organic liquids, noting the peculiarly conflicting statements of authorities regarding oxidation and decomposition during heating. Statements of Jungfleisch and Lefranc, Dieck and Tollens, Battmann, and others are not in accord regarding the decomposition of levulose at various temperatures.

The authors discussed the essential factors of the ideal dehydration method, stating these to be: (1) Homogeneity of liquids. (2) Uniform distribution of small quantities over large surfaces. (3) Uniform temperature. (4) Rapidity of dehydration.

"It has been found that as these conditions have been more perfectly attained, results have been more generally concordant. It may be said that, given a homogeneous liquid and uniformity of temperature, the method which insures wider distribution will provide greater rapidity of drying. Inasmuch as at a given temperature, alteration of the material will be proportionate to the time, results closer to the truth will be afforded by the method accomplishing the drying in shorter period."

The method devised by the authors is in accord with the above principles, and has been applied, so far, to the following range of materials: Heavy sorghum molasses, mixtures of sugar and levulose, milks, cream, maize juice (22 years old), beet juices, bonies, sorghum juices, commercial glucoses, and rosin turpentine solutions. The work on these materials covers over 4,000 determinations, in which the maximum variation in quadruplicates was 0.09 per cent., minimum 0.0, and mean 0.057 per cent. These results were obtained in from two to four hours, according to the character of the material.

The method is based upon the porosity of pumice stone, the

latter being crushed into fragments the size of a pea, strongly ignited, cooled, and the liquid to be dried, weighed from a pipette-weighing bottle, and uniformly distributed over the stone. The drying is conducted as usual.

The authors reserve the details of the method for future papers, work of a more complex character being now under way.

### *Discussion.*

Professor Wiley said the method had been proved accurate in giving duplicate results, although agreement is not proof of accuracy. The method could be used to determine matters volatile at 100°, chiefly water, as can be proved by passing them through sulphuric acid. Many of the substances to be dealt with contain levulose, and it is remarkable that we don't know just what takes place upon drying it, as the most opposite statements have been made. The determination of water is one of the most difficult things in agricultural chemistry, and this method is a step in advance. He referred to the fact that by the use of aluminum, flat dishes of wide expanse can be obtained.

Mr. Cutter stated that he had used practically the same method in the Utah Station, except that he had used the Hoffmeier capsules, and that the material, after being dried, could be utilized in other ways, especially the determination of fats in the analyses of meats. In his opinion, correct sampling of green material and the correct determination of moisture in original samples was, at present, one of the most perplexing problems with which agricultural chemists have to deal.

Professor Wiley said that green fodders should be shredded. The Laboratory of the Agricultural Department has the only shredding machine in the United States and it furnishes a good pulp.

Professor Seaman asked if the idea was to obtain a sufficient surface of pumice stone and was answered affirmatively.

W. D. Bigelow and E. E. Ewell called attention to a continuous extractor for large quantities of material. The apparatus consists of a percolator with slightly diverging sides, supported by an iron tripod, which in turn is placed in a shallow tray of enameled iron, or some other material which is not attacked by mercury. A crystallizing dish is placed below the percolator, and a bell-jar, with a reflux condenser attached, is placed over

the percolator, with its edges resting on the tray. The tray is then partially filled with mercury to prevent the escape of the ether.

January 10, 1895.

President W. H. Seaman in the chair; 14 members present;  
The following officers were elected:

*President*—Chas. E. Munroe.

*Vice-Presidents*—E. A. de Schweinitz and W. D. Bigelow.

*Treasurer*—W. P. Cutter.

*Secretary*—A. C. Peale.

*Additional Members of Executive Committee*.—H. W. Wiley, F. P. Dewey, F. W. Clarke, and W. H. Seaman.

#### CINCINNATI SECTION.

December Meeting.

Messrs. W. G. Wallace, Richard W. Proctor, George F. Feid, and Charles E. Jackson were elected to membership in the Section.

The election of officers for 1895 resulted as follows:

*President*—Karl Langenbeck.

*Vice-Presidents*—B. D. Westenfelder, and Irwin J. Smith.

*Treasurer*—Henry B. Foote.

*Secretary*—E. C. Wallace.

*Directors*—Dr. S. P. Kramer, Professor O. W. Martin, and H. L. Nickel.

Papers were read by Dr. S. P. Kramer on "Diphtheria Antitoxin," and Dr. Alfred Springer on "Elective Fermentation in Diabetes."

The following resolution was adopted:

*Resolved*, That the Cincinnati Section of the American Chemical Society respectfully recommends to the Committee on Nomenclature and Spelling of the JOURNAL of the Society, the use of the rules concerning the spelling of chemical terms recently adopted by the American Association for the Advancement of Science, limiting, however, the application of the rule concerning the spelling of *gramme* to articles in the field of medical or pharmaceutical chemistry.

Tuesday, January 15, 1895.

Vice-President Westenfelder in the chair.

Mr. F. Homburg and E. D. Frohman, recently elected members of the American Chemical Society, were elected to membership in the Section.

Mr. E. Twitchell read a paper on "The Separation of Solid and Liquid Fatty Acids." After reviewing the different methods of analysis of fats, Mr. Twitchell stated, that in his opinion, by precipitating all the solid and part of the liquid fatty acids from alcoholic solution by lead acetate (Jean's method) and determining iodine in a number of both original fatty acids and liquid acids left in the alcoholic solution, by calculation therefrom the amount of saturated and unsaturated fatty acids present in the fat could be determined with a fair degree of accuracy.

Dr. H. E. Newman read a "Report of Progress in Organic Chemistry," touching briefly upon L. Gatterman's method of reducing aromatic nitro compounds by a current of electricity; B. Tollens' work on the birotation of glucose; the synthesis of polyhydric alcohols by B. Tollens, H. Hosaus, and others, and Trillat's method of manufacturing dyes from formaldehyde and several amines, etc.

Reports of the Treasurer and Secretary, for 1894, were read and adopted. The Secretary's report showed an increase of six in membership, and that twenty papers had been read at the eight meetings held during the year.

---

#### LEHIGH VALLEY SECTION.

Thursday Evening, January 17, 1895.

The annual meeting was held at the Franklin House, Easton, Pa., six being present. A pleasant social time was spent, the only business transacted being the election of officers for the coming year. Messrs. Green and Brinker acted as tellers, and reported, on opening the ballots, the election of the following :

*Presiding Officer*—Edward Hart.

*Secretary*—Albert H. Welles.

*Treasurer*—Albert L. Colby.

*Executive Committee*—George P. Scholl, and J. W. Richards.

## Proceedings.

### COUNCIL.

January 23, 1895, the following resolution was approved by a majority of the Council:

*Resolved*, That the salary of the Editor for the year 1895 be fixed at two hundred and fifty dollars (\$250).

### CHANGES OF ADDRESS.

Blonin, R. E., 700 North St., Baton Rouge, La.  
Couch, Guy E., Swissvale, Allegheny County, Pa.  
Ewell, E. E., 2227 Fifteenth St., N. W., Washington, D. C.  
Field, Walter D., 4 Cedar St., New York City.  
Hahn, A. G. C., Nepera Chemical Co., Nepera Park, N. Y.  
Leighton, Virgil F., 1128 Ohio St., Lawrence, Kas.  
Marshall, G. D., 52 Cheshire St., Cleveland, Ohio.  
Miller, Chas. H., care of Baltimore Electric Refining Co., Keyser Building, Baltimore, Md.  
Redwood, Dr. Boverton, 4 Bishopgate St., Within, London, E. C., England.  
Weems, J. B., Iowa Agricultural College, Ames, Iowa.  
Wickhorst, Max, 2421 Dearborn St., Chicago, Ill.  
Williams, W. J., 635 Market St., Camden, N. J.

---

### MEETINGS OF THE SECTIONS.

#### CINCINNATI SECTION.

*Discussion of paper by E. Twitchell, read January 15, 1895.*

Dr. Newman asked Mr. Twitchell if he had ever mixed the pure solid and liquid fatty acids in the same proportion in which they were thought to exist in a given fat, and determined whether or not the iodine number of the mixture agreed with that of the fat.

Mr. Twitchell replied that he never had; he thought it was a good idea, but it was very difficult to obtain the liquid acids pure, and if obtained pure, on the slightest exposure to air, they would become more or less oxidized.

Replying to the question whether oleic acid could be obtained

pure, Mr. Twitchell said all fats contained linolic acid ; he had never found a fat which contained oleic acid free from linolic.

Professor Lloyd stated that he had once tried this separation of solid and liquid fatty acid by Muter's method. His experience led him to believe that lead stearate and palmitate were soluble in the lead oleate, and this mixture was soluble in ether. While pure lead stearate and palmitate might be nearly or quite insoluble in ether, in the presence of the oleate, ether would dissolve an appreciable amount. He would like to know what Mr. Twitchell considered the so-called pure oleic acid of the market to be.

Mr. Twitchell replying, said it was probably oleic acid with some oxidized acids.

Professor Lloyd then asked whether any method by means of which ten per cent. of cottonseed-oil could be detected in olive-oil existed.

Mr. Twitchell replied that he would not be positive about ten per cent., though possibly twenty per cent. could be detected ; he said the difficulty was due to the fact that oils contain all the fatty acids in different proportions, that two samples of pure oil might vary as much as the mixtures, so far as chemical composition was concerned they were the same.

Mr. Smith remarked that Dr. Stuerke had carried on a series of experiments for over a year, and had found that he could not differentiate less than ten per cent. of oils. Artificial lards are made on this basis.

Mr. Twitchell said that by treating a sample of olive-oil known to be pure, and an adulterated oil with sulphuric acid of given strength, he thought, after some practice, one ought to be able to detect five per cent. of cottonseed-oil.

---

#### RHODE ISLAND SECTION.

The regular monthly meeting of the Section was held at Providence, January 17, 1895.

President Charles A. Catlin in the chair.

Mr. Geo. F. Andrews read a paper upon **The Accuracy of the Fine Assay of Silver.**

The paper briefly discussed the general inaccuracy of the **fine** assay of silver, and the difficulty of getting a satisfactorily accurate assay of ores by the methods now in use.

It also discussed, in some detail, the losses in cupellation **due** to absorption and to volatilization. The effect upon the **button** of too great heat and too large amount of lead.

Mr. E. D. Pearce gave an interesting account of the **use of** hydrocyanic acid in destroying insects upon trees.

## Proceedings.

### COUNCIL.

The following persons have been elected by the Council to serve on the various standing committees for the coming year:

Committee on Nominations to Membership.—A. A. Breneman, P. T. Austen, and C. A. Doremus.

Committee on Finance.—Durand Woodman, A. P. Hallock, and A. H. Sabin.

Committee on Papers and Publications.—J. H. Long and E. F. Smith. Professor Smith desiring to be relieved from duty on this committee, the Council has elected Thomas B. Osborne to the vacancy.

Springfield, Mass., has been chosen as the place for the summer meeting.

### NEW MEMBERS ELECTED FEBRUARY 5.

Chesnut, V. K., Bio-Chemic Laboratory, U. S. Department of Agriculture, Washington, D. C.

Cobleigh, Wm. M., B.M., Agricultural College, Bozeman, Mont.

Desper, Ernest W., 37 Shelby St., Worcester, Mass.

Fields, J. W., 88 Wall St., New York City.

Lotz, Dumont, Portland, Ind.

Marshall, Geo. D., care of Newport Mining Co., Ironwood, Mich.

Murray, C. B., Braddock, Pa.

Penniman, Russell S., Lock P. O. Box 26, Dover, N. J.

Perry, Joseph H., 176 Highland St., Worcester, Mass.

Robbins, William K., Amoskeag Manufacturing Co., Manchester, N. H.

Rosengarten, Dr. Geo. D., 17th and Fitzwater Sts., Philadelphia, Pa.

Schloss, Joseph A., care of La Gran Fundision Nacional Mexicana, Monterey, Mexico.

Thiry, Joseph, care of Dr. G. E. Moore, 221 Pearl St., New York City.

Todd, Albert M., Kalamazoo, Mich.

Viall, William A., Brown and Sharp Manufacturing Co., Providence, R. I.

Woods, Henry, Wellesley, Mass.

#### ELECTED MARCH 1.

Bogardus, C. E., 60 Columbia St., Seattle, Wash.

Carlsson, Hugo, care of The Johnson Co., Johnstown, Pa.

Cox, W. Wetherill, 2025 Westmoreland St., Tioga, Phila.

Dobbin, Leonard, Chemistry Department, University of Edinburgh.

Dorset, Marion, Bio-Chemic Laboratory, Department of Agriculture, Washington, D. C.

Ehrenfeld, Augustus C., 15 West Monument Ave., Dayton, Ohio.

Ellis, G. H., Metropolitan Block, Chicago, Ill.

Jones, L. J. W., 1821 Arapahoe St., Denver, Col.

Keller, Charles, Wilkinsburg, Pa.

Mixer, Chas. T., 600 East High St., Ishpeming, Mich.

Thompson, Elihu, Lynn, Mass.

Tompkins, Vreeland, 553 Communipaw Ave., Jersey City, N. J.

Wagner, William G., 101 Leadenhall St., London, E. C., England.

#### ASSOCIATE ELECTED FEBRUARY 5.

Reubens, Charles M., 77 East 115th St., New York City.

#### CHANGES OF ADDRESS.

Coombs, Frank E., Natick, Mass.

Dewey, F. P., 621 F St., Washington, D. C.

Dodge, F. E., Box 85, Long Island City, N. Y.

Enequist, John, 136 Liberty St., New York City.

Hancock, David, Park View, Portsmouth, Va.



Stone, Edward P., Experiment Station, Durham, N. H.  
Townsend, Clinton, Barton P. O., La.  
Wrampelmeier, T. J., 909 Steiner St., San Francisco, Cal.

---

## MEETINGS OF THE SECTIONS.

### CINCINNATI SECTION.

February 15, 1895.

Dr. Alfred Springer in the chair.

A communication was read from Mr. John H. Westenhoff, stating his inability to be present, on account of a severe cold, and asking to have his paper on "Determination of Phosphorus in Ferro-Silicon" postponed to next meeting.

Professor Norton then stated that Mr. Robert Hochstetter, who was to read a paper on "The Souring of Milk," was detained at home by the serious illness of his business associate, Mr. L. W. Hoffman, and his paper would also have to be postponed.

Professor J. U. Lloyd spoke of the difficulty of obtaining distilled water which would meet the requirements of the U. S. Pharmacopeia, and described the apparatus he was having made consisting of a large copper still, a stone worm forty feet in length, and a stone receiver with stone stop-cock.

Dr. Springer said that absolutely pure distilled water could not be obtained in large quantities for technical use.

Professor Norton told of some interesting experiments carried on at the Laboratory of the University of Cincinnati, for the past five months, to determine the relative value of condensing-tubes made of block tin, aluminum, and glass. He said all glass was affected by water at high temperatures, and water distilled from glass vessels must, necessarily, be more or less contaminated; aluminum, owing to its high conductivity, made an excellent condensing-tube, and did not seem to be affected by water. Condensing-tubes of aluminum could also be used for distilling alcohol, ether, and many other liquids.

Chairman of Standing Committees were elected as follows:

Didactic, Physical, and Inorganic Chemistry, Dr. Alfred Springer, Chairman.

Organic Chemistry, Professor T. H. Norton, Chairman.

Analytical Chemistry, Lewis W. Hoffman, Chairman.

Medical, Physiological, and Biological Chemistry, Dr. S. P. Kramer, Chairman.

Technical and Pharmaceutical Chemistry, Professor J. U. Lloyd, Chairman.

On motion it was—

*Resolved*, That this Section respectfully recommend to the Committee on Publication of the Journal, the eminent desirability of having the leaves of the Journal cut before being sent to the members of the Society, as is the rule with the publications of the London Chemical Society and the Society of Chemical Industry.

---

RHODE ISLAND SECTION.

The regular monthly meeting was held at Providence, on the evening of February 23rd. Mr. Frank H. Andrews in the chair. Professor J. H. Appleton read a paper on Argon, presenting the facts as now known, and certain suggestions arising from them.

## Proceedings.

### BOARD OF DIRECTORS.

A charter for a Chicago Local Section was granted March 15.

### NEW MEMBERS ELECTED MARCH 22.

Catlett, Charles, 10 New Court House St., Staunton, Va.  
Frissell, W. I., 52 14th St., Wheeling, W. Va.  
Griffith, H. E., Oak Park, Cook County, Ill.  
Sharwood, W. J., University of California, Berkeley, Cal.  
Wait, Prof. Chas. E., Ph.D., University of Tennessee, Knoxville, Tenn.  
Williamson, G. N., 14 Dey St., N. Y. City.

### CHANGES OF ADDRESS.

Carlsson, Hugo, care of The Johnson Company, Lorain, Ohio.  
Clark, Dr. John E., 18 John R. St., Detroit, Mich.  
Couch, Guy E., 305 Mills St., Braddock, Pa.  
Guitermann, Franklin, 2815 Gilpin St., Denver, Colo.  
Hancock, David, care of Sloss Iron and Steel Company, Birmingham, Ala.  
Hazen, Allen, care of Noyes and Hazen, 85 Water St., Boston, Mass.  
Hoffmann, Philip C., care of The Chesapeake Guano Company, Equitable Building, Baltimore, Md.  
Howe, Frederic W., 9 Ashburton P. O., Boston, Mass.  
Keller, Chas., 113 Biddle Ave., Station D., Pittsburg, Pa.  
Simon, Dr. S. E., care of The Oscar A. Nenninger Company, Riverside Ave., near Second River, Newark, N. J.  
Waldbott, Dr. Sigmund, care of Messrs. Lloyd Bros., Court and Plum Sts., Cincinnati, Ohio.  
Weston, Robert Spurr, 21 Wyman St., Brockton, Mass.  
Wetmore, L. L., 35 Suffolk St., Holyoke, Mass.  
Zinsser, Fred. G., 197 William St., New York City.

## MEETINGS OF SECTIONS.

## CINCINNATI SECTION.

March 15, 1895.

Vice-President Irwin J. Smith presided.

A communication was read from the Globe Soap Company announcing the death of W. G. Wallace. The Secretary was instructed to express the sympathy of the Section to the family of the deceased.

Professor T. H. Norton then proposed the following resolution :

*Resolved*, That this Section of the American Chemical Society deploras the loss which it has suffered through the death of one of its most earnest and active members, Mr. Lewis William Hoffmann, Chairman of the Committee on Analytical Chemistry, which occurred at Cincinnati on March 4, 1895.

*Resolved*, That the Section expresses to the family of the late Mr. Hoffmann its deep sympathy with them in their sudden bereavement.

Mr. John H. Westenhoff read a paper on the "Determination of Phosphorus in Ferro-Silicon." Mr. Westenhoff had experienced great difficulty in dissolving ferro-silicons in nitric or hydrochloric acid or aqua regia. He found by adding a small quantity of hydrofluoric acid to either nitric or hydrochloric acid, solution could be readily effected, and the determination could then be carried on by the usual method. Very satisfactory results were obtained and the time was shortened to that required for phosphorus determinations in pig iron.

Mr. Robert W. Hochstetter read a paper on "The Souring of Milk." He ascribed the souring of milk to the presence of bacteria and showed the chemical changes that took place. Results of analyses of a sample of milk, a portion of which was analyzed each day for five days, showed the amount of total solids decreased, the per cent. of fat was constant, while the acidity was variable and not proportional to the length of time milk had been standing. Electric discharges, produced over the surface of the milk for several hours, seemed to have little or no effect, and Mr. Hochstetter thought the souring of milk during thunder storms was due to the fact that the atmospheric condi-

tions were more favorable to the growth of the bacilli. He found that milk cooled quickly, as soon as drawn from the mammary gland, was not liable to sour during thunder storms.

Mr. E. Twitchell was elected Chairman of the Committee on Analytical Chemistry to fill the vacancy caused by the death of Lewis W. Hoffmann.

---

#### WASHINGTON SECTION.

Thursday, February 14, 1895.

President Charles E. Munroe in the chair.

The meeting was devoted mainly to the address of the retiring President, Dr. Wm. H. Seaman. His subject was "Chemistry in Education," which was considered under four heads: (1) What is chemistry, (2) what are its relations to common life, (3) how much chemistry is actually taught in our schools, and (4) what should be taught there. After the delivery of the address, it was resolved to co-operate with the other scientific societies in enlarging the powers of the joint commission, and the adoption of a constitution for the joint commission based upon its being composed of the officers and administrative boards of the several component societies.

Thursday, March 14, 1895.

President Charles E. Munroe in the chair; thirty-five members present; Mr. G. E. Barton was elected to membership.

Professor F. W. Clarke gave a brief account of his general theory concerning the constitution of the silicates. His work will appear in full as a bulletin of the U. S. Geological Survey. Parts of it have already appeared in this JOURNAL.

Dr. H. N. Stokes read a paper on the "Chloronitrides of Phosphorus and the Metaphosphimic Acids." The paper was a contribution to the subject of homology and polymerism of inorganic compounds. It was shown that Liebig's chloronitride of phosphorus,  $P_3N_3Cl_3$ , is but one member of an homologous series of chloronitrides, having the general formula  $(PNCl_2)_x$ , two others of which were described; *viz.*,  $(PNCl_2)_1$ , and another of

unknown molecular weight. The chloronitrides  $(\text{PNC}_x)_n$  and  $(\text{PNCl}_x)_n$ , by saponification, yield trimetaphosphimic acid,  $(\text{PNO}_x\text{H}_x)_3$ , and tetrametaphosphimic acid,  $(\text{PNO}_x\text{H}_x)_4$ , which may be regarded as members of an homologous series of acids parallel with the metaphosphoric acid series, and having one-third of the oxygen of the latter replaced by the amide group. These acids being derived from chlorides containing the nuclei  $(\text{PN})_x$  may be regarded as polymers of the simplest form  $\text{PNO}_x\text{H}_x$ , in which nitrogen atoms serve as connecting links between the phosphorus atoms.

Dr. J. E. Blomén read a paper "On the Manufacture of Soluble Nitrocellulose for Nitrogelatine and Plastic Dynamite."

## Proceedings.

### BOARD OF DIRECTORS.

A Charter for a Nebraska Local Section was granted April 15, 1895.

The following act was passed by the Senate and Assembly of New York, and approved by the Governor April 18, 1895:

#### CHAPTER 346.

##### *An Act for the Relief of the American Chemical Society.*

The people of the state of New York, represented in the Senate and Assembly, do enact as follows:

SECTION 1. It shall be lawful for the American Chemical Society to elect its Directors without any restriction as to their residence or citizenship, except such as may be imposed by the by-laws of said Society now in force; or as such by-laws may be amended hereafter.

SECTION 2. Said Society may hold its meetings at such times and places in this state, or elsewhere, as it may select, and all acts done without this state shall have the same force and effect as if done within this state.

SECTION 3. This act shall take effect immediately.

---

### COUNCIL.

The Council has approved the election of Edward Hart as Editor for 1895.

A majority of the Council have also approved the time and place suggested for the summer meeting; *vis.*, Springfield, Mass., August 27 and 28, 1895.

#### NEW MEMBERS ELECTED APRIL 8.

Bachman, Irving A., Augusta, Ga.

Blasdale, W. C., 2111 Channing Way, Berkeley, Cal.

Emery, William O., Chicago Athenaeum, Chicago, Ill.

Harding, E. P., Univ. of Minnesota, Minneapolis, Minn.

Hooland, H. B., Univ. of Minnesota, Minneapolis, Minn.

Lenher, V., State University, Berkeley Cal.

O'Neill, Prof. Edmond, State University, Berkeley, Cal.

Shepherd, R. S., Univ. of Minnesota, Minneapolis, Minn.

Strathern, F. P., Univ. of Minnesota, Minneapolis, Minn.

Tinsley, John D., Miller School, Crozet, Va.

**ASSOCIATE ELECTED APRIL 8.**

**Smith, Thorn, Agricultural College, Mich.**

**ELECTED APRIL 9.**

**Davidson, G. M., 317 Linden Ave., Oak Park, Cook Co., Ill.**  
**Ferry, Charles, 309 2nd St., Troy, N. Y.**  
**Hornbeak, S. L., 578 60th St., Chicago, Ill.**  
**Ikuta, Massuo, Univ. of Chicago, Chicago, Ill.**  
**Redding, Clifford R., Chem. Lab. U. P. Ry., Omaha, Neb.**  
**Riggs, Prof. R. B., Trinity College, Hartford, Conn.**  
**Seamon, F. H., Guanacevi, Est. de Durango, Mexico**  
**Smoot, Albert M., 9 Cliff St., N. Y. City.**  
**Wells, Horace L., Sheffield Scientific School, New Haven, Conn.**

**ELECTED APRIL 19.**

**Hall, Clarence A., 3220 Powelton Ave., Philadelphia.**  
**Lasher, Frederick G., 76 Newell St., Brooklyn, N. Y.**  
**Roegner, Edward W., 200 Jefferson Ave., Passaic, N. J.**

**CHANGES OF ADDRESS.**

**Burleigh, Wm. F., care of West Bergen Steel Works, Jersey City, N. J.**  
**Chase, Geo. W., 526 Quincy Ave., Scranton, Pa.**  
**DeChalmot, Dr. G., care of Willson Aluminum Co., Spray, Rockingham Co., N. C.**  
**Hand, Daniel, 62 East Park St., Newark, N. J.**  
**Hine, S. K., Poland, Ohio.**  
**Morgan, F. M., Longue Pointe, Hochilaga Co., Canada.**  
**Starr, H. F., 142 4th Ave., Newark, N. J.**  
**Waterman, C. N., Room 65, 620 Atlantic Ave., Boston, Mass.**

---

**MEETINGS OF SECTIONS.**

**NEW YORK SECTION.**

**The regular meeting was held at the Chemical Lecture Room of the Columbia College School of Mines, on April 12, Prof. Peter T. Austen in the chair. Fifty members were present. Minutes of March meeting were omitted owing to the absence of**



the Secretary, Prof. Morris Loeb. Mr. W. S. Myers was appointed secretary *pro tem*. Messrs. Richards & Co. exhibited a number of interesting forms of novel and improved apparatus including microscopes, polariscopes, aluminum ware, chemical preparations, etc. Dr. Ernest E. Smith read a paper on the Theories of the Chemical Pathology of Uraemia, describing the history and development of the various theories and giving details of experiments showing the extent of the toxic effect of urea. He held that the products of the disease are factors of varying proportions in producing the observed symptoms and effects. Prof. Charles A. Doremus, and Dr. E. R. Squibb discussed the paper. Prof. Charles F. Chandler gave a very interesting talk on Chemical Manufacture in Europe, and discussed in detail the latest processes for manufacturing sodium, aluminum, chlorine, caustic soda, coal-tar colors, and pharmaceutical preparations, which he had personally studied during a recent trip abroad. The speaker emphasized the general prosperity of the chemical industry in Germany, and also drew attention to some of the recent industrial developments in this country, in particular that of carborundum.

Dr. W. D. Horne read a paper on the "Decarbonization of Bone-Black," establishing by a number of experiments the claims for the immense saving which may be effected by decarbonizing the char in the newly patented Weinrich Apparatus. A discussion followed, in which Dr. Chandler and F. O. Mattheisen took part. Prof. Chandler asked if the amount of nitrogen in the char before and after decarbonization in the apparatus had been tested, to which Dr. Horne replied that it had not been.

Dr. Peter T. Austen explained the production of two new solid coloring matters from logwood, which he had recently patented, one of which was made by the action of ammonium carbonate upon logwood extract of high gravity, and which appeared to consist of ammonium compound of haematine, and differed from the oxidized logwood extract made by him at an earlier date by the action of sodium nitrite upon logwood extract. The other product was produced by the action of borax of high gravity logwood extract. It was stated that borax seemed to have a peculiar action on the extract of logwood,

which was not produced, so far as the speaker knew, by any other substances. The borax derivative differed from the others in not being fully oxidized, and hence contained both haemateine and haematoxylin, so that it resembled in composition the logwood extract.

The chairman stated that he was happy to announce that the society would soon be able to have quarters of its own, as two available rooms were now under consideration, and that the informal dinners would be resumed with the next meeting.

The society then adjourned.

---

#### WASHINGTON SECTION.

Thursday, April 11, 1895.

President Charles E. Munroe in the chair. Fifty-three present. Dr. J. E. Blomen was elected to membership.

Mr. H. C. Sherman read a paper on "The Determination of Nitrogen in Fertilizers." Mr. Sherman stated that in determining nitric nitrogen in fertilizers containing notable quantities of chloride, the results were always too low. He obtained much better results by slightly modifying either the modified Kjeldahl or Gunning methods. In the modified Kjeldahl method Mr. Sherman recommends that the sulphuric and salicylic acid mixture be cooled before it is added to the substance under examination, and that the substance be digested in this mixture in the cold for some time before the addition of the reducing agents.

In the Gunning method Mr. Sherman obtains satisfactory results by boiling for thirty to forty minutes after the liquid has become entirely colorless.

Professor C. E. Munroe exhibited specimens of calcium carbide and discussed its value from theoretical and practical standpoints. He also generated acetylene by the decomposition of this substance with water, and showed the properties of the flame formed by its combustion. The paper was discussed by Messrs. Chatard, Clarke, and Dewey. Professor Clarke called attention to the theoretical interest of the substance. He said that calcium carbide was an interesting connecting link between organic and inorganic chemistry, the hydrogen of acetylene being

replaced by a divalent metal, and being introduced into the molecule again by the simple decomposition of water. He called attention to the fact that calcium carbide is merely an example of a series, and referred to the strontium and barium carbides of Moissan.

Mr. E. G. Runyan and Professor Wiley read a paper on "Precipitation of Small Quantities of Phosphoric Acid by Ammoniacal Citrate of Magnesium."

The principle of the method developed in the paper is based upon the observation that with quantities of phosphoric acid below five per cent., the direct citrate method gives entirely too low results. An attempt was made to remedy this source of error by adding in such cases a known volume of phosphate solution of ascertained strength in order to bring the total amount of phosphoric acid up to fifteen per cent. or more. Large numbers of analytical data were shown, illustrating the fact that by this fortification, perfectly accurate results could be obtained by the citrate method, even in samples containing a fraction of one per cent.

Professor Munroe then led in the discussion of the topic of the evening, "Can Argon be Accepted as a New Element," and reviewed the work of Rayleigh and Ramsay, Crookes and Olzewski, on this subject. Prof. Clarke stated that he had received a letter from Prof. Ramsay a few days before, asking for a sample of the uraninite in which Dr. Hillebrand reported nitrogen. Reviewing the work of Dr. Hillebrand, he said that in dissolving uraninite in sulphuric acid, he noticed that a gas was liberated steadily and uniformly throughout the whole operation. Nitric acid and ammonia were both prepared from this gas, and its spectrum was considered to be that of nitrogen, although there were some lines in the spectrum which did not belong to that of nitrogen, and were supposed to be caused by the presence of some impurity. Prof. Ramsay, in working with Cleveite, from Norway, observed a gas whose spectrum showed the more prominent argon lines, and also lines which have been ascribed to the solar element helium. The residues from Dr. Hillebrand's samples have been sent to Prof. Ramsay. Prof. Clarke said that this gas had not been found in uraninite con-

taining thorium, and suggested the possibility that the argon was combined with uranium in uraninite. Attempts would be made, he said, to combine argon with uranium.

Dr. Chatard said that it was his recollection that Dr. Hillebrand's nitrogen was very difficult to oxidize, and that the amount of oxidation products obtained was barely sufficient for their identification.

Dr. Stokes said that at Dr. Hillebrand's request, he had examined a sample of uraninite, and had not been able to detect nitrogen by the ferrocyanide reaction.

The president said that the literature of nitrogen was being reviewed, and all statements that could have any bearing on argon or which would seem to refer to argon in any way, were being noted.

---

#### CINCINNATI SECTION.

Tuesday, April 16, 1895.

Prof. T. H. Norton, gave a very interesting account of "Recent Important Discoveries in Chemistry," dwelling particularly upon the commercial importance of calcium carbide for the production of acetylene, with a practical demonstration of the value of acetylene as an illuminant.

Papers on "Stereoisomeric Compounds of Nitrogen," by Dr. H. E. Newman, and "The Adulteration of Powdered Elm Bark," by Henry B. Foote, were postponed to next meeting.

## Proceedings.

### COUNCIL.

An invitation from Cleveland, Ohio, to hold the winter meeting at that place has been accepted by Council.

#### NEW MEMBERS ELECTED APRIL 29.

Adgate, Matthew, B.S., P. O. Box 32, Bridgeport, Conn.  
Blalock, Thomas L., B.S., 908 Canton St., Baltimore, Md.  
Dal Molin, A.A., 41 Barclay St., New York City.  
Emerson, W. H., Ph.D., Ga. School of Tech., Atlanta, Ga.  
Hinds, Prof. J. I. D., Ph.D., Cumberland University, Lebanon, Tenn.  
Koebig, Julius, Ph.D., 1824 Ellis St., San Francisco, Cal.  
Maas, Philip, 1228 West College Ave., Philadelphia, Pa.  
Miller, Dr. Stephen C., Columbian University, Washington, D. C.  
Priest, Prof. Henry, Canton, N. Y.  
Slocum, J. W., 514 Gay St., Knoxville, Tenn.

#### ELECTED MAY 16.

Keiser, Dr. E. H., Bryn Mawr, Pa.  
Ledoux, Albert R., M.S., 9 Cliff St., New York City.  
MacDowell, Wm. F., Ph.D., U. S. Immigration Service, Med. Dept., Ellis Island, N. Y.  
Porter, John Bonsall, Glendale, Ohio.  
Salisbury, Jerome H., M.D., 982 Adams St., Chicago, Ill.  
Tuthill, J. B. T., Salem Gas Light Company, Salem, Ore.  
Walker Henry V., Ph.D., 32-34 Clinton St., Brooklyn, N. Y.  
Waters, A. A., A.M., Abingdon, Ill.

#### ASSOCIATE ELECTED MAY 16.

Harris, Henry H., Ph.D., Taylor, Pa.

**CHANGES OF ADDRESS.**

Burrell, Loomis, Little Falls, N. Y.  
Endemann, Dr. Herman, 23 William St., New York City.  
Furgeson W. C., 40 North Parsons Ave., Flushing, N. Y.  
Graham, Wm. H., 5 Valley Place, Upper Montclair, N. J.  
Kellar, Chas., 113 Biddle Ave., Station D, Pittsburg, Pa.  
Krause, Dr. O. H., Prospect Ave., Hackensack, N. J.  
McDermot, Thomas E., Washington Ave. above 20th St.,  
Philadelphia, Pa.  
Saarback, Dr. Ludwig, 23 William St., New York City.

---

**MEETINGS OF THE SECTIONS.**

**LEHIGH VALLEY SECTION.**

The regular monthly meeting was held at Lehigh University, South Bethlehem, on the evening of May 2. There were fourteen present. Porter W. Shimer read a paper on the "Determination of Graphite in Pig Iron," and Albert L. Colby followed with a talk on "The Selection of Samples for Analysis." He suggested that instruction in sampling be given to undergraduates as a regular part of their training, and that uniform methods of sampling be adopted by practical chemists.

## Proceedings.

### COUNCIL.

A committee consisting of Professors Hale, Austen and Brene-man, has been appointed by the President to consider the question of a permanent badge for the Society.

#### NEW MEMBERS ELECTED JUNE 6.

Beal, Prof. James H., Scio College, Scio, Ohio.  
Chauvenet, Wm. M., 709 Pine St., St. Louis, Mo.  
Fuller, Geo. W., Experiment Station, Lawrence, Mass.  
Gaylord, Wallace R., 146 Terrace Drive, Pasadena, Cal.  
Harrison, John B., Government Laboratory, Georgetown,  
Demerara, British Guiana.  
Hengstler, Louis, Jr., Hoboken, N. J.  
Howard, Chas. D., S.B., Newport, R. I.  
Lagai, P. G., Ph.D., 17 Park Place, New York City.  
Linebarger, C. E., South Division, High School, Chicago, Ill.  
McBryde, J. Bolton, University of Tenn., Knoxville, Tenn.  
McClure, Prof. Edgar, University of Oregon, Eugene, Ore.  
Pagelson, Otto H., 2421 Dearborn St., Chicago, Ill.  
Peacock, Samuel, 47 South 17th St., Philadelphia, Pa.  
Rich, H. L., Lasell Seminary, Auburndale, Mass.  
Richardson, Geo. M., Stanford University Cal.  
Wellington, Harry T., Wellington Manufacturing Co., 468  
and 470 Cherry St., New York City.

#### CHANGES OF ADDRESS.

Barba, W. P., 5110 Newhall St., Germantown, Phila., Pa.  
Brown, Lucius P., 150 North Cherry St., Nashville, Tenn.  
Behr, Arno, 171 Grand Ave., Pasadena, Cal.  
Benton, Geo. W., High School, Indianapolis, Ind.  
Bird, Herbert S., care of N. Y. Tartar, Co., 9th St. and  
Gowanus Canal, Brooklyn, N. Y.  
Cambier, Jacob, 1000 Abriendo Ave., Pueblo, Colo.  
Carpenter, Thos. B., 325 Jersey St., Buffalo, N. Y.  
Chase, Geo. W., Thomas, Ala.  
Clapp, Geo. H., 325 Water St., Pittsburg, Pa.  
Collins, W. H., 6757 Perry Ave., Chicago, Ill.  
Clymer, Edwin S., 45-47 Reed St., Reading, Pa.

- Doolittle, O. S., 130 North 5th St., Reading, Pa.  
 Evans, Thomas, Chemist American Cotton Oil Co., 46 Cedar St., New York City.  
 Feid, George F., 199 Findlay St., Cincinnati, Ohio.  
 Hochstetter, Robert W., Oak and Bellevue Sts., Mt. Auburn, Cincinnati, Ohio.  
 Linn, A. F., Park Place, Springfield, Ohio.  
 Lustig, A. L., P. O. Box 582, Providence, R. I.  
 Maxwell, Dr. Walter, Sugar Experiment Station, Honolulu, S. I.  
 Nichols, Wm. H., 47 Cedar St., New York City.  
 Pearce, Edward D., care of L. P. Shepard and Co., Providence, R. I.  
 Powell, J. W. Bureau of Ethnology, Washington, D. C.  
 Rosengarten, Geo. D., 1700 Fitzwater St., Philadelphia, Pa.  
 Schimpf, Henry W., 365 Franklin Ave., Brooklyn, N. Y.  
 Simonson, W., 901 Race St., Cincinnati, Ohio.  
 Smith, Thorn, Agricultural College, Lansing, Mich.  
 Stone, W. G., 302 Union St., Brooklyn, N. Y.  
 Taylor, Thomas, M.D., 238 Massachusetts Ave., N. E., Washington, D. C.  
 Waller, Elwyn, 440 First Ave., New York City.  
 Wesson, David, University Heights, N. Y.  
 Wickhorst, Max H., 268 Forquer St., Chicago, Ill.  
 Wood, E. F., Munhall, Pa.  
 Wood, Edward S., 688 Boylston St., Boston, Mass.  
 Wulf, Henry C., care of Pacific Mill Co., San Francisco, Cal.  
 Youmans, W. J., 72 Fifth Ave., New York City.

## MEETINGS OF THE SECTIONS.

### RHODE ISLAND SECTION.

The March meeting was held Thursday evening, March 21. J. P. Famworth, Esq., read a paper on the "Selection of Water for Bleaching and Other Manufacturing Purposes."

The April meeting was held Thursday evening, April 23. Mr. H. S. Bingen presented a paper entitled "A Resumé of the Methods of Bleaching Cotton Piece Goods."

The May meeting was held Thursday, May 23. Edward D. Pearce, Esq., presented a paper on "Pollen." The paper contained suggestions as to the nature of the color of pollen grains, with a review of methods of mounting, and the effect upon the coloring-matter of various mounting media. The paper was



illustrated by twenty-five typical slides exhibited under the microscope.

The June meeting was held Thursday, June 13th, 12 m. This being also the Annual meeting, the first business was the election of officers for the ensuing year, which resulted as follows: Presiding Officer, Mr. Charles A. Catlin; Secretary and Treasurer, Prof. Walter M. Saunders; Member of the Executive Committee, Mr. George F. Andrews.

After the transaction of other business relating to the work of the Section for the coming year, the Chairman presented his annual address, taking as his topic, "Chemical Laboratory Microscopy," advocating a more thorough training of young chemists in microscopy, specially and directly applied to chemical laboratory work. Presenting and discussing recent advances in micro-physiography, crypto-chemistry, and micro-chemical reactions, he described and illustrated some original methods and apparatus of his own, more particularly a method of mounting for the purpose of localizing the individual particles in samples of powdered material, by means of adhesive films upon slides having engraved or etched numbered squares, thus fixing each in certain definite portions for purpose of subsequent identification through optical behavior, physical form, or reaction with reagents. He further suggested and illustrated the valuable service that may be obtained from cultures of some of the lower organisms in the classification of turbid solutions, more especially, the removal of suspended finely divided carbon, such as at times results from the carbonizing of organic matter in the presence of fluxing and other salts, the suspended matter of such solutions being attracted and entangled in the mycelium of the fungus growth induced therein, and thus with it easily removed. He finally discussed micro-chemical reactions in their bearing upon qualitative chemical analysis, urging a more complete classification of the facts relating to reactions already studied, with the view of elaborating a less complicated scheme of micro-chemical analysis than any suggested, commending the works of Klément and Rénard, of Haushofer and of Behrens, as worthy of confidence. In his own work he found the greatest usefulness of micro-chemical analysis, not in any scheme, but as auxiliary

to the ordinary course of qualitative analysis, through special reactions curtailing oftentimes to a remarkable degree its tedious separations, and further, finding in it an approximate qualitative value far exceeding the indications of ordinary qualitative work in this direction; and suggested possibly the attainment of very close approximations quickly, by comparison of reactions with standards of known value.

During an intermission, the members in attendance enjoyed a delightful lunch in one of the private dining rooms of the famous Hope Club.

---

CINCINNATI SECTION.

The meeting was held Wednesday, May 15, Dr. Alfred Springer presiding.

Mr. Henry B. Foote read a paper on "The Adulteration of Powdered Elm Bark." He stated that in his opinion the microscope was the only reliable means of detecting adulterations in the powdered bark. He thought no reliance should be placed on the starch test, as the liber of young trees contained starch but no reaction could be obtained from bark from old trees.

Prof. T. H. Norton read a paper on "Ammonium Thioacetate." After speaking of the many advantages of this over hydrogen sulphide as a precipitant, he demonstrated practically the ease with which the arsenites and arsenates could be completely precipitated from solution.

Adjourned until October 15.

## Proceedings.

### CHANGES OF ADDRESS.

Dorr, John V. U., care of D. & D. Smelting Co., Deadwood, S. D.

Emery, Sidney S., care of Repauno Chem. Co., Chester, Pa.

Girling, R. N., 2728 Prytania St., New Orleans, La.

Howard, C. D., Durham, N. H.

Howe, Fred. W., 53 Monument Ave., Charlestown, Mass.

Kenan, Wm. R., Jr., Univ. of N. C., Chapel Hill, N. C.

Lammers, Theo. L., 32 Pittsburg Block, Helena, Mont.

Neiman, Howard S., 8 East 97th St., New York City.

Newman, H. E., 261 Central Ave., Cincinnati, O.

Seamon, W. H., School of Mines, Socorro, New Mexico.

Starke, Frederick W., 4169 Leidy Ave., West Philadelphia, Pa.

Wardman, Geo. B., care of La Gran Fundicion, Central Mexicana, Agnos Calientes, Mexico.

White, Annie E., 71 Forest Ave., Buffalo, N. Y.

---

### MEETINGS OF THE SECTIONS.

#### CHICAGO SECTION.

At a meeting held June 3, in the chemical lecture room at the Northwestern University, School of Pharmacy, the Chicago Section of the American Chemical Society was organized with the following officers: Frank Julian, President; J. C. Foye, Vice-President; F. B. Dains, Secretary; J. H. Long, Treasurer. Executive Committee, Frank Julian, A. L. Smith, and F. B. Dains.

The Section then adjourned until the regular meeting in September.



## Proceedings.

### ELEVENTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

#### MINUTES.

The Eleventh General Meeting of the American Chemical Society was held in Springfield, Mass., August 27 and 28, 1895.

The meeting was called to order in Evangelist Hall, at 10 A. M., August 27, by the President, Professor Edgar F. Smith of Philadelphia.

President Smith introduced Mayor Charles L. Long, of Springfield, who spoke a few words of welcome to the Society, as follows:

"Mr. President and Members of the American Chemical Society. I cannot claim that the words I shall speak to you will rise to the dignity of an address. It was suggested to me that I should welcome the Society to Springfield, and this I most cordially do.

This is an occasion of great interest to our people. Nothing like it has occurred since the meeting of the American Association for the Advancement of Science here in 1859. You have met as the representatives of a great branch of science.

If I were called upon to name that branch of science that has accomplished the most practical results for mankind, I should say chemistry. The debt of gratitude that humanity owes to chemistry can never be repaid. Look at the results it has secured. Take for example, the Chemistry of Agriculture, it has made the earth to yield bountiful harvests. Then, too, the matter of foods and the preparation of foods for human consumption. Chemistry has given to the world the means for detecting the adulteration of foods. There is hardly an article that forms the dress of man or woman that does not owe its value to the skill of the chemist. In medicine, chemistry has done great service to man in providing cures for the various ills of the human body. For this mankind cannot be too grateful.

When the sun has set beyond the western hills and darkness has come on, you will find that the chemist has turned night into daylight in giving us the products of petroleum and illuminating gas, whether obtained from the destructive distillation of coal, or by the decomposition of steam. And so throughout the realm of human wants.

Why, then, should I not welcome to the city of Springfield, the representatives of a branch of science to which mankind is indebted more than to any other of the various branches of science? I trust your stay will be pleasant and that your deliberations will be profitable, and that after partaking of the hospitalities here, you will safely return to your respective homes."

President Smith, in behalf of the Society, replied:

"Mr. Mayor: In response to your very cordial invitation to come and take possession of the land, as it were, permit me to return the hearty thanks of the Society. We anticipate much pleasure and profit in our visit to this progressive city, known throughout the land as the place where so many scientific appliances are utilized. We shall gladly avail ourselves of the opportunities you offer.

In bidding us welcome to your city, you introduce to your fellow citizens the representatives of the youngest national chemical society, national in that its representatives are found in the east, the west, the north and the south. In recent years, also, the names of prominent European chemists have appeared upon our roll. Our object is to bring together all who cultivate the science of chemistry. In our membership of about one thousand, there are found many engaged in agriculture, in botany, in the iron industry, in coloring, and last but not least, the ubiquitous teacher of chemistry.

This Society fosters research, research not only in one direction, but in all. We have chemists interested in every department of chemistry. In this respect the American Chemical Society is unique, it stands alone. The great object of this Society is to make the science of chemistry in every way helpful to our fellow men.

Permit me, in advance, to thank you for the many hospitalities of which we shall be the recipients. We have nothing to offer in return unless you shall feel inclined to remain with us and listen to our papers and discussions."

At the conclusion of these remarks the President announced that the Society was ready for the presentation of papers and called upon Dr. W. A. Noyes, who read a paper on the "Determination of the Heating Effects of Coal," prepared by himself in conjunction with J. R. McTaggart and H. W. Craven. Dr. Noyes' paper was discussed by Drs. Hart and Prescott, after which Prof. F. P. Venable presented a paper entitled "A Case of Mistaken Identity." There was a short discussion on the paper by Drs. Hart and Prescott and President Smith, followed by a few remarks by the author.

The next paper was upon "The Possibility of the Occurrence of Hydrogen and Methane in the Atmosphere," by Prof. Francis C. Phillips. This was discussed by Drs. W. A. Noyes, Edward Hart and E. E. Smith. Then R. P. Williams presented a paper on "A new Electrical Process for Making White Lead," which was discussed by Messrs. Meyers, Prescott, Hart, E. F. Smith and T. H. Norton.

Dr. A. A. Noyes read a paper on "The Electrolytic Reduction of Paranitro Compounds in Sulphuric Acid Solutions," and this was followed by another paper by the same author on "The Occurrence of Trimethylene Glycol as a By-Product in the Glycerol Manufacture." There were some discussions and questions on the last paper by Messrs. W. A. Noyes and A. B. Prescott, and a brief reply by the author.

An informal report of the present condition of the Society was given by the General Secretary, who announced the establishment of two local sections since the last meeting, one in Nebraska, with headquarters at Lincoln, Nebr., and the other in the city of Chicago. The membership of the Society was stated to be just 900. There are also some persons who have been elected but have not yet qualified, and quite a number of persons whose applications for membership have been favorably reported by the Standing Committee on Nominations to membership, so that practically the number of members may be considered as about 950.

The following named members have died since the report given at the last General Meeting:

Dr. A. A. Fesquet, Dec. 26, 1894.  
 Prof. H. B. Nason, Jan. 17, 1895.  
 J. C. Dittrich, (drowned on the Elbe) Jan. 1895.  
 W. H. Whalen, Feb. 3, 1895.  
 Prof. Mark Powers, Mar. 1, 1895.  
 Lewis Hoffman, Mar. 4, 1895.  
 Dr. Gideon E. Moore, April 15, 1895.  
 W. G. Wallace, April, 1895.  
 Wm. C. Wilson, April 16, 1895.

There are now eight Local Sections of the Society; *viz.*, Rhode Island, Cincinnati, New York, Washington, Lehigh Valley, New Orleans, Nebraska and Chicago.

A bill was passed by the legislature of the State of New York during its last session, allowing the Society to elect its directors without regard to their residence or citizenship, and legalizing all action of the Society that may be taken at any of its meetings outside of the State of New York. Prof. F. W. Clarke, chairman of the committee appointed to consider the question of amendments to the constitution, has resigned, and Dr. H. W. Wiley has been appointed to fill the vacancy.

After the report by the General Secretary and certain announcements regarding excursions, visits, and sessions of the Society, a paper on "The Determination of Sulphur in Refined Copper," by George L. Heath, was read by Dr. Wm. McMurtree, the author being absent. The morning session was then adjourned.

In the afternoon the chemists made an excursion to Holyoke, leaving Springfield at 1 P. M. and returning in time for the evening session. At Holyoke they visited the mills of the Holyoke Paper Company, the Merrick Thread Company, and the Farr Alpaca Company.

At 1 P. M. under the guidance of Messrs. H. H. Bosworth, C. M. Kirkham, J. Eastman Belding and H. S. Anderson of the Local Committee, the chemists took the electric car for Holyoke. They visited first the mills of the Holyoke Paper Company. Mr. Oscar Greenleaf, Treasurer of the Company, conducted the party through the building and explained to them very clearly and minutely the various steps in the manufacture of paper from the beginning to the end.

The company use both American and foreign rags. The rags are first dusted in a star-shaped holder, which, by its revolution, allows the rags to fall down from one star-point to another thus driving out the dust which escapes through the meshes of the sieve-like sides of the holder.

After being dusted the rags are placed upon tables where they are picked over by hand, and buttons, hooks and eyes, pieces of whalebone, rubber, etc., are removed, scythes being used to cut them off when possible. Sometimes valuable articles are found and these the workers are allowed to keep. This furnishes a valuable incentive for the careful examination of the rags. After the first picking-over the rags are examined again by another person and any remaining objectionable articles removed, and the rags are also sorted into different grades. The rags are then passed between closely fitting cogs which tear them into shreds,



after which they are chopped into small pieces by an instrument in which the knives revolve in a manner similar to those of a lawn mower. After this the rags are sometimes subjected to another process of dusting by being whipped while in a suitable receptacle.

They are then put into large revolving cylinders and boiled under pressure of thirty-five to fifty pounds in milk of lime of about the consistency of cream. After being thus treated sufficiently they are removed, the lime allowed to drain off, and the rags are then put into washing engines, where they are reduced to pulp, a stream of clear spring water flowing in and a stream of dirty water flowing out continuously at the other end of the washing machine.

The rags are reduced to pulp by the scraping action of steel bars, those of one set passing through the narrow spaces between the others and thus drawing out the fiber somewhat like the process of scraping cloth for lint. When the rags have been reduced to pulp and sufficiently washed, a solution of chloride of lime is run in for the purpose of bleaching the pulp. At this stage the flow of water in and out of the vat is checked, as is also the pulp-reducing action of the machine, and the mechanical action is simply such as to keep the bleaching pulp stirred and rotating around in the vat of the machine.

After being bleached the pulp is allowed to flow into draining rooms, *i. e.*, into large receptacles containing a perforated bottom, where it remains from five days to three or four weeks, according to the requirements. The chloride-of-lime water is there drained off.

The bleached and drained pulp is then put into beating engines, where it is washed with water to remove any remaining chloride of lime, and if necessary, sodium hyposulphite is added to neutralize the last traces of the chloride. It is here reduced to a very fine fiber. Then it is put into a large tank and pumped on to a paper machine having a large endless piece of wire cloth, which is drawn along and carries with it the fiber thinned with a sufficient amount of water. In this operation the cloth is given a shaking motion, and as the water runs off the fibers are shaken closely together, interlaced more or less, and packed down so as to cohere into one continuous sheet. The remaining water, so far as possible, is withdrawn from the fiber by a suction pump.

From the wire cloth the paper passes between heavy rollers and upon a sheet of woolen felt. Thence it goes over iron cylinders heated inside with steam. After the paper is thus dried, it is passed through a solution of glue or extract of rawhide. This animal sizing is thus absorbed by the paper, some vegetable sizing having been already introduced into the material in the beating engine. The vegetable sizing is resin. The paper, wet with animal sizing, is hung over poles where it dries slowly. If rapidly dried, the strength of the glue is partly destroyed.

When dried, the paper is calendered. There are two methods of calendering: (1) the American, by which the paper passes between rolls,

three of chilled iron and two of paper arranged alternately; (2) the foreign, by which the paper is pressed between two heavy chilled rolls after having been packed in layers between zinc or pasteboard plates.

The best quality of paper is not weighted. No weighting is done at the mills of the Holyoke Paper Co. Whenever weighting is done at all, the weighting—or filling—material is introduced into the heating engines with the pulp.

Mr. O. S. Greenleaf, Treasurer of the Holyoke Paper Co., in addition to his other many courtesies, sent to the General Secretary a package containing a sample box of paper and envelopes for each of the chemists who had visited their mill. These were not received until after the adjournment of the meeting and some of the chemists had left the city, but the boxes were distributed to all who were still accessible and the General Secretary, in behalf of the members, sent a letter to Mr. Greenleaf, expressing their cordial thanks for this pleasing souvenir of their visit.

The evening session on Tuesday, Aug. 27, was held in room 6 of the High School, President E. F. Smith presiding. A paper upon "The Speed of Oxidation by Chloric Acid," prepared by Dr. R. B. Warder and Herman Schlundt, was read by Dr. Warder and afterwards discussed by Drs. Norton, A. A. Noyes and Warder. This was followed by a paper on "The Reaction between Copper and Concentrated Sulphuric Acid," by Chas. Baskerville. The subject of Mr. Baskerville's paper was discussed by Dr. Andrews, after which a few words of reply were offered by the author.

The closing paper of the evening session was read by Prof. Francis C. Phillips. The subject of the paper was, "The Evolution Method for the Determination of Sulphur in Iron." After the reading of the paper the subject was discussed by Dr. Hart, and then after some announcements by the Secretary, the evening session was adjourned.

The Society assembled for its morning session Aug. 28, at 9 A. M. in Evangelist Hall, President Smith in the chair. Dr. Norton read a paper upon "The Use of Aluminum for Condensers," and this was discussed by Drs. Hale, McMurtrie and others. A paper upon "Arsenic in Glycerol," prepared by Geo. E. Barton, was read by Dr. McMurtrie in the absence of the author. The subject was discussed by Messrs. Prescott, W. P.

Mason and Munsell. Then followed a paper presented by Mr. Lyman F. Kebler on "The Acidimetric Estimation of Vegetable Alkaloids." This paper elicited considerable discussion, the following named gentlemen taking part: Messrs. Prescott, W. A. Noyes, Sabin, W. P. Mason, Bigelow, Munsell, Andrews and Kebler.

The next paper was upon "Metaphosphinic Acids and their Derivatives," by Henry N. Stokes, and a few remarks were made upon this paper by Dr Norton. Chas. H. Herty then presented a paper on "Observations on Double Platinum Salts." This was discussed by Messrs. Stokes, Howe, W. P. Mason and Myers, after which Dr. Launcelot W. Andrews read a paper on "The Analysis of Alloys containing Tin, Lead and Antimony.

After the General Secretary had made some announcements, Wm. K. Robbins described a new burette holder, designed by himself, and Dr. A. A. Noyes announced the publication of the "Review of American Chemical Research," and distributed specimen pages of the periodical to the members present. Prof. W. P. Mason described a new kind of water-bath. Dr. Hart, in the absence of the author, read a paper upon "Tellurium, its Separation from Copper Residues, with Notes on some New Reactions," prepared by Cabell Whitehead.

President Smith then invited Prof. E. W. Morley, President of the American Association for the Advancement of Science, to address the Society. Dr. Morley in reply made some informal remarks, summing up the results of investigations that have been made upon the "Atomic Weight of Oxygen," which, by any reasonable system of averaging the results of all of the most reliable investigations, was shown to be 15.879. President Smith thanked Prof. Morley very heartily for his remarks, and in most complimentary terms showed how the chemists of America are to be congratulated upon having among their number, one whose own research upon the atomic weight of oxygen would rank among the most profound and reliable investigations that have ever been made upon that subject by any scientist of any country.

Dr. A. B. Prescott said, "I can add nothing to the words

already spoken in congratulation to this Society and to this meeting, words most fit to be spoken at this time, in all of which I desire most sincerely to join. If I would add another word to express what has been in my heart as we sat here, it would be a word of acknowledgment for us all, of what we owe to our presiding officer in this meeting. He has conducted our discussions with equal interest and spirit in all subjects, suggesting fruitful inquiry and saving the valuable time of the meeting, crowded as it has been with papers and living topics. I am sure I can speak for every member of the Society in giving thanks to both the General Secretary and the President for their tireless and effective service in preparing for this meeting and conducting it throughout."

Drs. Hart and Norton followed briefly with similar remarks, and upon motion of Dr. Hart, the Society passed a vote of thanks to the President and General Secretary in harmony with the sentiments that had just been expressed.

Upon motion of the General Secretary the thanks of the Society were extended to the Local Committee of Arrangements in Springfield for their untiring efforts to make the meeting of the chemists a pleasant and successful one, and especially to the Local Secretary, Mr. Wm. A. Webster. Also to Prof. Wm. Orr, Jr., Chairman, and Mr. Henry H. Bosworth, Secretary of the Committee on Excursions; to Mr. C. M. Kirkham, Mr. J. Eastman Belding, and Mr. H. S. Anderson; to the officers of the Holyoke Paper Company for permission to visit their mills and to Mr. O. S. Greenleaf, Treasurer of said Company, and Mr. C. J. Humes-ton; to the Farr Alpaca Company, and especially to Mr. H. M. Farr, Agent, and Mr. F. H. Metcalf, Superintendent; to the Merrick Thread Company, and especially to Mr. O. H. Merrick, Superintendent, and Mr. S. M. Bentley; to the United Electric Light Company, the Hampden Paint and Chemical Company, and to the officers in charge of the United States Armory, especially to Col. Alfred Mordecai, Major W. H. Rexford and Lieut. Tracy C. Dickson, for their personal and official courtesies; to the hotels and railroad companies for reduced rates; to the local press for their careful and complete reports of the meeting, and to the citizens of Springfield generally for their many

hospitalities and their efforts to make our visit to their city pleasant and our meeting successful.

The remaining visits to be made by the chemists were announced, after which the Eleventh General Meeting of the Society was formally adjourned.

According to the announcements made the members visited the United States Armory and the Hampden Paint and Chemical Works during the afternoon, and early the following morning those who cared to go were very courteously received at the plant of the United Electric Light Company by Mr. H. S. Anderson, electrician, who conducted them through the works and showed them many very interesting experiments with high tension currents. This formed a very fitting termination of one of the most enjoyable and successful meetings the Society has ever held.

The following members registered in attendance at the meeting:

Edgar F. Smith, Philadelphia, Pa.  
 Albert C. Hale, Brooklyn, N. Y.  
 Wm. McMurtrie, Brooklyn, N. Y.  
 Edward Hart, Easton, Pa.  
 Wm. Bromwell, Port Deposit, Md.  
 W. D. Bigelow, Washington, D. C.  
 A. H. Sabin, New York.  
 Wm. Frear, State College, Penna.  
 Francis C. Phillips, Western Univ., Allegheny, Pa.  
 Rufus P. Williams, English High School, Boston.  
 Robt. B. Warder, Washington, D. C.  
 Frank N. Guild, Greensboro, Vt.  
 A. F. Linn, Wittenberg College, Springfield, O.  
 Fred. W. Morse, N. H. Expt. Sta., Durham, N. H.  
 Arthur A. Noyes, Mass. Inst. of Tech., Boston, Mass.  
 J. A. Deghueue, Brooklyn, N. Y.  
 W. A. Noyes, Terre Haute, Ind.  
 Mary Engle Pennington, Philadelphia, Penna.  
 Elizabeth A. Atkinson, Three Tuns, Penna.  
 E. W. Allen, Washington, D. C.  
 Alfred H. Mason, New York.  
 J. B. Lindsey, Amherst, Mass.  
 A. B. Prescott, Ann Arbor, Mich.  
 F. P. Venable, Chapel Hill, N. C.  
 Ernest Ellsworth Smith, New York.

Frank D. Maine, Springfield, Mass.  
Otis C. Johnson, Ann Arbor, Mich.  
Thomas H. Norton, Cincinnati, O.  
Chas. Baskerville, Chapel Hill, N. C.  
J. Bird Moyer, Univ. of Penna., Philadelphia.  
C. Smith Boynton, Burlington, Vt.  
B. B. Ross, Auburn, Ala.  
B. W. Kilgore, Raleigh, N. C.  
Francis E. Bates, Westfield, —.  
John A. Myers, Morgantown, W. Va.  
Charles L. Parsons, Durham, N. H.  
William P. Mason, Troy, N. Y.  
Alfred Springer, Cincinnati, O.  
Launcelot Andrews, Iowa City, Ia.  
Lyman B. Hall, Haverford, Pa.  
L. P. Strong, Springfield, Mass.  
Leslie A. Cooper, Springfield, Mass.  
Wm. Woodhouse, North Adams, Mass.  
P. H. Rolfe, Lake City, Fla.  
F. Atwood Serrine, Jamaica (L. I.) N. Y.  
Geo. W. DeWolf, Springfield, —.  
Chas. H. Herty, Athens, Ga.  
Lyman F. Kebler, Philadelphia, Pa.  
Charles E. Munsell, Brooklyn, N. Y.  
T. R. White, New York.  
George D. Gable, Fairfield, Iowa.  
Jas. Lewis Howe, Washington and Lee Univ., Lexington, Va.  
W. K. Robbins, Manchester, N. H.  
H. N. Stokes, Washington, D. C.  
Walter E. Smith, Providence, R. I.  
W. O. Atwater, Middletown, Conn.  
Charles E. Munroe, Washington, D. C.  
Edward W. Morley, Cleveland, Ohio.  
Mrs. E. F. Smith, Philadelphia, Pa.  
E. D. Campbell, Ann Arbor, Mich.  
Mary F. Leach, Mt. Holyoke College, S. Hadley, Mass.  
Paul C. Freer, Ann Arbor, Mich.  
Clara A. Pease, High School, Hartford, Conn.  
Frank E. Coombs, Natick, Mass.  
E. Twitchell, Cincinnati, O.

ALBERT C. HALE,  
General Secretary.

## NEW MEMBERS ELECTED SEPT. 21.

Ando, Shinichi, care of Apollo Iron and Steel Co., Apollo, Pa.  
 Carnell, Wm. C., lab. Ill. Steel Co., So. Chicago, Ill.  
 Crane, Wm. H., M.D., 92 W. 7th St., Cincinnati, O.  
 DeFremercy, J. L., 44 Broadway, N. Y. City.  
 DeRoode, Rudolf, care of Fraser & Co., 262 5th Ave., N. Y. City.  
 DuPont, Francis G., Wilmington, Del.  
 Johnson, Jesse F., care of Hamilton Powder Co., Montreal, Can.  
 Macadam, Wm. Ivison, Surgeon's Hall, Edinburgh, Scotland.  
 Swett, Charles E., 23 Bolander St., Providence, R. I.  
 Thackray, George E., Cambria Iron Co., Johnstown, Pa.

## ASSOCIATE ELECTED SEPT. 21.

Read, Frederick, 140 Nassau St., N. Y. City.

## CHANGES OF ADDRESS.

Allen, W. N., 2 Chestnut St., Philadelphia, Pa.  
 Barton, G. E., Columbian Univ., Washington, D. C.  
 Brinker, Harry L., 811 West Federal St., Youngstown, O.  
 Chase, George W., Bellwood, Pa.  
 Dewey, F. P., 702 Ninth St., N. W., Washington, D. C.  
 Fuller, Fred D., 7 Dix St., Worcester, Mass.  
 Gudemann, Edw., Davenport, Iowa.  
 Hand, Daniel, Edison Lamp Works, Harrison, N. J.  
 Hershey, A. N., care of A. L. Thomsen, Mfg. Chemist, Baltimore, Md.  
 Hoffman, Philip C., care of Georgia Chemical Works, Augusta, Ga.  
 Innes, Murray, care of Old Dominion Copper Co., Globe, Arizona.  
 Lammers, Theodore L., Townsend, Montana.  
 Leighton, Virgil L., Tufts College, Mass.  
 Linebarger, C. E., 2601 Calumet Ave., Chicago, Ill.  
 Loeb, Dr. Morris, 112 N. 72d St., New York City.  
 Meeker, G. H., care of Andover Iron Co., Phillipsburg, N. J.  
 Mellen, E. D., 9A Forest St., N. Cambridge, Mass.  
 Peacock, S., care of Nolan Pub. Co., P. O. Box 2113, Philadelphia, Pa.  
 Pemberton, H., Jr., 2027 Spruce St., Philadelphia, Pa.  
 Puckner, W. A., 73 Wells St., Chicago, Ill.  
 Seamon, F. H., Apartado 101, Matehuala Est San Luis Potosi, Mexico.  
 Seher, August, 115 Chestnut St., Newark, N. J.  
 Trimble, Henry, 145 N. 10th St., Philadelphia, Pa.  
 Wesson, David, The Wesson-Nivison Mfg. Co., Cortlandt, N. Y.

## MEETINGS OF THE SECTIONS.

### RHODE ISLAND SECTION.

The first meeting of the new year, 1895-96, was held at Providence, Thursday evening, Sept. 26, 1895. Prof. J. H. Appleton, of Brown University, gave an address on "Sugar and Sugar Refining," illustrated by about sixty slides shown by the lantern. Many of the slides were from negatives taken in remote sugar-producing countries, *e. g.*, Sandwich Islands, South Africa, and of course, Cuba.



## Proceedings.

### NEW MEMBERS ELECTED OCT. 10.

Browne, Arthur Benjamin, 119 Water St., Boston, Mass.  
Burt, M. C., Amherst, Mass.  
Chamberlain, Geo. D., care of Iroquois Furnace, S. Chicago, Ill.  
Johnson, Edward S., Park Bros. & Co. Steel Works, 33d and  
Smallman Sts., Pittsburgh, Pa.  
Lindsey, J. B., Ph.D., Expt. Station, Amherst, Mass.  
Louderbeck, Harry C., Griffin Wheel Co., Chicago, Ill.  
Lovejoy, Ellis, Union Furnace, Ohio.  
McCrae, John, Ph.D., Univ. of Cincinnati, Cincinnati, Ohio.  
Noyes, Dr. Arthur A., Mass. Inst. of Tech., Boston, Mass.  
Sanborn, E. R., Sharon, Pa.  
Taylor, Edward R., S. B., Cleveland, Ohio.  
Underwood, Edward L., Canton, Mass.  
Wakeman, Alfred J., 819 Madison Ave., N. Y. City.  
Withers, W. A., Raleigh, N. C.

### CHANGES OF ADDRESS.

Couch, Guy E., Pottsville, Pa.  
Drown, Thomas M., South Bethlehem, Pa.  
Fuller, Geo. W., Box 614, Louisville, Ky.  
Hornbeck, S. L., Tehuacana, Texas.  
Linn, Prof. A. F., Wittenberg College, Springfield, O.  
Moale, Philip R., care of N. Y. and Boston Dyewood Co., Green  
and West Sts., Greenpoint, Brooklyn, N. Y.  
Nicholson, Edward E., 716 University Ave., S. E., Minneapolis, Minn.  
Pearce, Edward D., care of T. P. Shepard & Co., Box 1336,  
Providence, R. I.  
Sherman, H. C., 252 W. 53d St., New York City.

---

## MEETINGS OF THE SECTIONS.

### LEHIGH VALLEY SECTION.

The Fall meeting of the Lehigh Valley Section was held at Bethlehem, October 10. Thos. Tyrer, President of the Society of Chemical Industry of England, was the guest of the Section,

and he was accompanied from New York by representatives of the New York Section of the Society of Chemical Industry and the New York Section of the American Chemical Society, in a parlor car, kindly provided by the Lehigh Valley Railroad. It had been hoped that Ludwig Mond, F. R. S., who accompanied Mr. Tyrer to America, would also be present, but he was prevented by business engagements.

Reaching Bethlehem at 10.30 A. M., the party inspected the works of the Bethlehem Iron Co., and the officials took them through every department of the government plant. After visiting the laboratory, which through the labors of Albert L. Colby, formerly chemist, now metallurgical engineer, and C. A. Buck, chief chemist, is probably the best equipped in its facilities for doing rapid work of any in the country. The company provided their guests with a dinner served in the works offices, to which forty-two sat down.

The stated meeting was held at 4.30 P. M., Prof. Edward Hart, presiding officer in the chair.

Albert L. Colby read a paper on the "Rapid Methods perfected in the Laboratory of the Bethlehem Iron Co., and in Use There." At the close, he presented each member with a novel souvenir, a nickel-plated armor plate washer manufactured by the company, on which was stamped the date and place of meeting of the Section and the name of the person to whom it was presented. In the centre was engraved, "Accurately analyzed for carbon in 12 minutes, Manganese in 10 minutes, Phosphorus and Silicon in 30 minutes."

Other papers were read as follows: "Chemical vs. Bacteriological Examination of Water." Prof. Wm. P. Mason, of Troy, read by Dr. Wm. McMurtrie. "On Standardization of Iodine Solution," by G. H. Meeker." "A Device for Sampling Metals," by Porter W. Shimer."

Following the reading of papers, interesting responses were made by Thos. Tyrer, Esq., Alfred Mason, and Peter T. Austen. The New York delegation made the return trip at 6.30 P. M., and the meeting was voted to be the most successful one in the history of the Section.

ALBERT H. WELLES, Secretary.

## CINCINNATI SECTION.

A meeting of the Cincinnati Section was held on October 15.

Dr. Alfred Springer presented "A Tribute to Pasteur," and papers were read on "The Laboratory Uses of Aluminum" and "Recent Progress in Theoretical Chemistry" by Prof. T. H. Norton.

Dr. John McCrae, instructor in chemistry, University of Cincinnati, and Prof. A. F. Linn, professor of chemistry, Wittenberg College, Springfield, O., were elected members of the Section.

## RHODE ISLAND SECTION.

A meeting of the Rhode Island Section was held at Providence on Thursday evening, Oct. 17, 1895, Chairman C. A. Catlin, presiding.

Dr. H. J. Wheeler, of the Rhode Island Agricultural Experiment Station, read a paper upon "Acidity of Soils and its Relation to the Growth of Agricultural Plants and to the Development of the Potato Scab."

Attention was called to the fact that though the mention of sour soils appears to be almost universal, it is but rarely that any writer on agricultural chemistry has called attention to the fact that upland, light, and naturally well-drained soils are ever so acid as to be injurious to the growth of plants, and then generally, only where acidity was concluded. Instances of the occurrence of a degree of acidity in soils of this character sufficient to be injurious to many agricultural plants were cited from places in Massachusetts, Maryland, and Kingston, West Kingston, Westerly and Hope Valley, R. I. Acidity apparently of an equal degree, has been observed in many other places in New England where the effect of the same has not yet been established by actual experiments. In the course of the experiments at the R. I. Agricultural Experiment Station, covering a period of three years, over ninety varieties of plants have already been employed. The most marked differences in the effect of acid soils before and after liming have been observed in connection with plants which have ordinarily been grouped as requiring similar soil and fertilization. Photographs were shown illustrating that the presence of carbonates or the existence of acidity in soils has a wonderful

effect upon the development on potato tubers of the bacterioid fungus which causes the potato scab. The necessity for acid tests in soils of the above-mentioned character, particularly when derived from certain granites and mica schists, was strongly emphasized.

## Proceedings.

### COUNCIL.

The following have been approved by the Council :

*By-Law.*—If any member who is already a Councilor or Director shall be elected to an office which makes him *ex-officio* a Councilor or Director, the acceptance of such office shall be considered to involve the resignation of his former position as Councilor or Director, and the position so vacated shall be filled in the manner prescribed by the constitution.

*Resolution.*—Ordered that the dues for membership for 1896 be collected by the General Secretary as in the current year, and that he be allowed 10 per cent. on all collections as compensation for his work.

Cleveland has been designated as the place for the coming annual meeting, to be held on Monday and Tuesday, December 30 and 31, 1895.

The bill of the Chemical Publishing Co. for \$256.95, for the October number of the Journal, has been approved.

#### NEW MEMBERS ELECTED NOVEMBER 2, 1895.

Asbury, S. E., West Raleigh, N. C.  
Atkinson, Miss Elizabeth A., 125 W. Tulpehocken St., Germantown, Philadelphia, Pa.  
Best, Otto, Ph.D., care N. Y. Tartar Co., 9th St. and Gowanus Canal, Brooklyn, N. Y.  
Bizzell, J. A., West Raleigh, N. C.  
Conklin, E. S., care S. S. White Dental Mfg. Co., Prince's Bay, Staten Island, N. Y.  
Dow, Allan Wade, District Building, Washington, D. C.  
Hall, Clarence A., 3220 Powelton Ave., Philadelphia, Pa.  
Hayes-Campbell, J., 327 Washington, St., Newport, Ky.  
Hollick, Herbert, Easton, Pa.  
Lewis, Gerald, Box 70, South Bethlehem, Pa.  
Love, E. G., Ph.D., 80 East 50th St., N. Y. City.  
Ludlow, Gabriel, Sharpsville, Pa.  
Mallory, J. Halsey, 361 Monroe St., Brooklyn, N. Y.  
Semans, Wm. O., Delaware, Ohio.  
Shepherd, Frank I., Kyle, Ohio.  
Way, A. B., New Brunswick, N. J.  
Wentworth, Walter V., Ticonderoga, N. Y.  
Williams, Herbert M., B.S., 124 St. James Place, Brooklyn, N. Y.

ASSOCIATES ELECTED NOVEMBER 2, 1895.

Church, Herbert Kenneth, 112 Martien Hall, Lafayette College, Easton, Pa.  
Hopkins, N. Monroe, 1730 I St., N. W., Washington, D. C.  
Louder, J. Willis, South Easton, Pa.  
Parker, W. F., New Brunswick, N. J.  
Sigman, Alfred S., Easton, Pa.  
Thatcher, Charles J., Easton, Pa.

CHANGES OF ADDRESS.

Behr, Arno, 2266 Second St., San Diego, Cal.  
Bolton, H. Carrington, Cosmos Club, Washington, D. C.  
Dains, F. B., 2421 Dearborn St., Chicago, Ill.  
Ford, Allen P., care of Crane Co., 12th and Canal Sts., Chicago, Ill.  
Forrest, Chas. N., Room 462, Central Power Sta., 14th and Penna. Ave., Washington, D. C.  
Guild, Frank N., Wesleyan Univ., Middletown, Conn.  
Harrison, Herbert E., Box 15, Trenton, Mich.  
Herrick, Wm. Hale, 207 Greenwich St., New York City.  
Hodge, H. B., 1300 Pennsylvania Ave., Washington, D. C.  
Mallory, J. Halsey, 539A Green Ave., Brooklyn, N. Y.  
Tucker, Francis T., 1720 M St., Lincoln, Neb.

---

MEETINGS OF THE SECTIONS.

CHICAGO SECTION.

A meeting of the Chicago Section of the American Chemical Society was held October 15.

A Note on the precipitation of zinc in acid solution was presented by Prof. J. B. Nagelvoort.

Dr. J. H. Long gave the results of some experiments on the precipitation of antimony cinnabar from solutions of tartar emetic by means of sodium thiosulphate.

Mr. C. L. Kennicott read some correspondence between Alfred Allen and Mr. Bannister, of Somerset House, Eng.

NEW YORK SECTION.

The October meeting of the New York Section was held in the University Building, Prof. P. T. Austen in the chair.

Prof. Austen was re-elected Presiding Officer for the ensuing year. Dr. Durand Woodman was elected Secretary and Treas-

surer. Profs. A. H. Sabin, A. C. Hale and A. R. Leeds were elected as Executive Committee. Messrs. McKenna and Hale were elected to act with the chairman as delegates to the Council of the Scientific Alliance. Prof. Hale reported for the delegates to this Council for 1894-95. On motion, his report was accepted.

The chair appointed a committee of two to act with the New York Section of the Society of Chemical Industry in giving a complimentary dinner to Messrs. Tyrer and Mond.

The chairman also appointed a committee to draw up suitable resolutions upon the death of Pasteur, the same to be signed by the Chairman and Secretary and forwarded to the French Chemical Society. Messrs. Squibb and Loeb were appointed.

A paper on "Progress of Chemical Work in the Agricultural Experiment Station," was read by E. B. Voorhees; "On the Development of Colors on Vegetable Fibers," by Dr. Baker; "A Laboratory Note Book," "Cold Production of Oxygen," "A Specimen Bottle," and "The Commercial Production of Haematein," by Prof. P. T. Austen; "Quantitative Volumetric Determination of Orcinol," by H. S. Neiman.

The meeting of November 8th was held in the hall of the Mott Memorial Library at 64 Madison Ave., New York, Prof. P. T. Austen in the chair.

The minutes of the previous meeting were read and approved.

The Secretary reported that the letter authorized to be prepared in regard to the death of Louis Pasteur, had been received from the Committee, and duly forwarded to the French Chemical Society.

Prof. W. P. Mason's paper on "The Chemical vs. the Biological Examination of Water" was read by Prof. McMurtrie, in the absence of the author.

In the discussion which followed, the opinion was general, that to arrive at a sound conclusion, it is necessary to make both examinations, and in addition, the history of a water should be known as accurately as possible.

Prof. McMurtrie stated that in examining a large number of wells in the State of Illinois, he had found no cases of typhoid fever from the use of well waters in which the nitrites, free and albuminoid ammonia were all low.

These determinations, in conjunction with careful investigation of the history of a water he had found a pretty safe guide to an opinion.

Dr. Horne described an interesting case of large increase of nitrites in mixing three water supplies, the nitrites being low in each of the waters tested separately. Prof. Speyers suggested that the presence of hydrogen sulphide, or other reducing agent in one of the waters, acting on nitrates in the others might account for this phenomenon.

A paper "On the Heat of Solution of Certain Carbon Compounds" was read by Prof. C. L. Speyers.

Dr. Austen read a "Note on Runge's 'Bildungstrieb' of Substances" and exhibited a copy of this old and rare work.

Mr. Cutts read a paper by T. S. Gladding, "On the Gravitimetric Method of Determining Phosphoric Acid by the Phosphomolybdate Method."

"Specimens showing the Effects of Gun-Cotton Explosions" were exhibited by Mr. W. H. Burleigh.

The meeting was then adjourned to the second Friday in December.

#### WASHINGTON SECTION.

The Washington Section of the American Chemical Society held a meeting on May 9th, President Munroe in the chair. Forty members were present. Marion Dasett and S. C. Miller were elected to membership.

The first paper was read by Dr. E. A. de Schweinitz on a new Meteorite from Forsyth County, N. C. The second was by Dr. Peter Fireman, on "Hydrogen Fluoride Poisoning." Discussion by Messrs. Munroe, Brown and Chatard. Prof. Munroe thought that cases like that of Dr. Fireman should be brought together in order that similar accidents could be guarded against and remedies provided. Mr. Brown referred to a work in French upon such accidents; Dr. Chatard referred to similar experiences of his own with hydrogen fluoride. The next paper was by Dr. W. H. Seaman, on "Progress in the Manufacture of Artificial Musk." He stated that the artificial product is a commercial article, and traced its history from the time it was first prepared in 1759 by Markgrof down to the present time, refer-



ring to the different patents issued for artificial musk. The one most known is the Musk Bauer. None of the compounds are in any specific sense artificial musk. A large number of nitro bodies possess valuable odors and synthetic chemistry is trying to supplant the natural bodies. In the manufacture of soap the artificial substance is extensively used.

The subject for discussion for the evening was "The Chemical Action of Micro-organisms." Dr. de Schweinitz opened the discussion by referring to the difficulty of treating the subject in a limited time, and spoke of the vast number of micro-organisms by which changes in the mineral, animal and vegetable kingdoms are produced and of the very few that up to the present time had been isolated and studied. He then described the substances resulting from the fermentations of glucose alcohol and the part played by the different germs in these fermentations and of their selective action. Different germs acting upon the *same* substance produce different results, and the same germ acting upon *different* substances produce the same results. The products of pathological bacteria are complex and difficult to isolate, but it is to them that the fatal effects of diseases are to be attributed. The poisonous products belong for the most part to the toxins that have been isolated from cultures of the different bacilli: tetanus, cholera, diphtheria, tuberculosis and glanders. The albuminoids for the most part are rich in phosphorus, and seem to be more nearly like the nucleins. The quantity produced is so extremely small that it is difficult to make absolute identifications, but they are extremely virulent even in most minute quantities. The pathological power of germs is often decreased or diminished; they become attenuated and are no longer fatal in their effects, either because they do not find the soil adapted to their multiplication or because the amount of active poison secreted is too small. The germs are interesting also on account of the composition of their own bodies; this is constant, but different for different forms. The proximate constituents are varied. For instance, the percentage of fat is very different in the different bacilli. Some of the germs produce cellulose and others do not. The different effects produced by them must result from the internal structure of the molecules.

Surgeon General Sternberg, who was present as a guest, gave a brief outline of some of the products of pathological bacteria, referring to the work of Brieger, Pfeiffer, Kitasato and others. The toxins may be acids or bases unstable, or united with the colloid bodies. "Toxalbumens" may be continued as the term to apply to them.

Prof. Wiley said that micro-organisms were at work in the interest of the farmer long before there were any medical schools. He referred to the intimate relations that existed between certain minute organisms and the chemical reactions which take place in the soil.

Prof. George P. Merrill, who was present as a guest, was called upon and said that he was not quite so enthusiastic as Dr. Wiley upon the part micro-organisms played as rock destroyers. They have been found in rocks that are highly decomposed, but he thought it had not been proved that they caused the decomposition. He looked at the subject from a conservative standpoint, partly from the fact that it is one that few geologists have investigated. In the District of Columbia he thought mechanical agencies were more potent than chemical action as rock destroyers. Rocks that disintegrated to the depth of fifty feet lost three per cent. or less of their original constituents. The disintegration goes to the depth of 200 feet. He thought the action of bacilli has been overestimated.

The Society at 10 P. M. adjourned until November.

#### CINCINNATI SECTION.

A meeting of the Cincinnati Section was held on November 15, 1895, Dr. Alfred Springer presiding.

In an interesting talk on "The Glycerol Industry," Mr. Joseph Feenster described the various processes that have been used in the manufacture of glycerol and exhibited samples representing different stages of the process, and the several grades of glycerol now on the market.

In a paper on "The Recent Progress in Cellular Chemistry," Dr. S. P. Kramer gave a resumé of the latest advances in micro-chemical work.

Mr. F. I. Shepherd, of this city, and J. Hayes-Campbell, of Newport, Ky., were elected members of the Section.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

---

### ON THE BEHAVIOR OF ALLYLMALONIC, ALLYLACETIC, AND ETHYLIDENEPROPIONIC ACIDS WHEN BOILED WITH CAUSTIC SODA SOLUTIONS.

CONTRIBUTIONS TO THE KNOWLEDGE OF PROPYLIDENEACETIC  
ACID.<sup>1</sup>

BY JOHN G. SPENZER.

Received October 26, 1894.

DURING the preparation of hydropiperic acid, Fittig and Buri,<sup>2</sup> in 1883, discovered that in the reduction of piperic acid by means of sodium amalgam, two very different isomeric hydropiperic acids were formed, according as the reducing fluid was kept almost neutral, or allowed to become strongly alkaline by not adding acid. In the first procedure they obtained the already known and now designated  $\alpha$  hydropiperic acid, while in the second process together with the  $\alpha$  acid, larger or smaller quantities of the new isomeric  $\beta$  hydropiperic acid appeared, which seemed to have been produced from the  $\alpha$  acid through the agency of the caustic soda formed in the reducing fluid.

In fact it was proven experimentally, by heating the  $\alpha$  hydropiperic acid, with caustic soda on the water-bath, that  $\beta$  hydropiperic acid could be obtained.

Weinstein<sup>3</sup> and Regel<sup>4</sup> were induced by Fittig to examine the two isomeric acids further, and because of its behavior on substituting bromine and hydrobromic acid as also in the oxidation with potassium permanganate they came to the interesting con-

<sup>1</sup> Read before Section C., American Association for Advancement of Science, Brooklyn, N. Y., August 20, 1894.

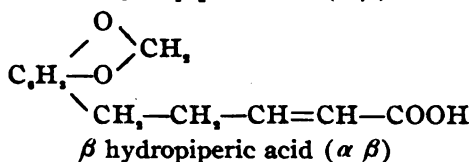
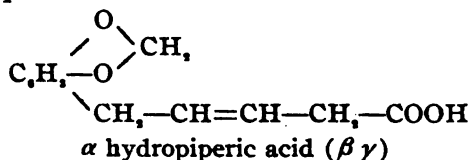
<sup>2</sup> *Ann. Chem.*, 216, 171.

<sup>3</sup> *Ibid.*, 227, 31.

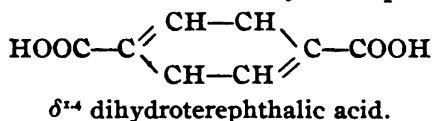
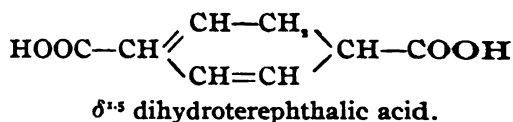
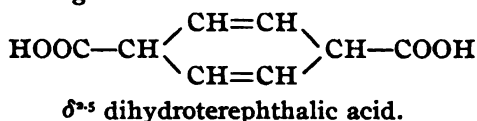
<sup>4</sup> *Ber. d. Chem. Ges.*, 20, 414.

clusion that the  $\alpha$  hydropiperic acid was a  $\beta \gamma$  unsaturated acid, and that the  $\beta$  hydropiperic acid must be an  $\alpha \beta$  unsaturated acid.

Therefore, by the conversion of the  $\alpha$  hydropiperic acid into the  $\beta$  hydropiperic acid, under the influence of hot caustic soda, a moving of the double bond of union towards the carboxyl group takes place as follows:

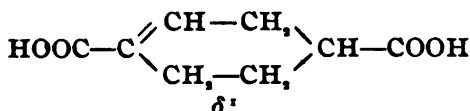
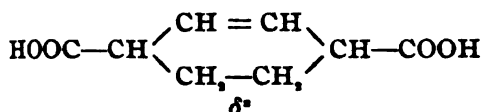


Other such displacements of the double bonds of union through the agency of alkalies and even by boiling water were soon found. Baeyer<sup>1</sup> observed, that the  $\delta^{2,5}$  dihydroterephthalic acid, became the  $\delta^{1,5}$  dihydroterephthalic acid, when boiled with water, and the latter, in turn, when boiled with caustic soda, produced the  $\delta^{1,4}$  dihydroterephthalic acid, according to the following scheme:

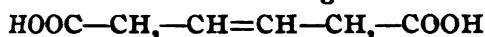


Further  $\delta^2$  tetrahydroterephthalic acid when treated with hot caustic soda produces  $\delta^1$  tetrahydroterephthalic acid as follows:

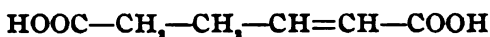
<sup>1</sup> *Ann. Chem.*, 251, 257,



Finally hydromuconic acid according to Baeyer and Rupe<sup>1</sup> by the same treatment is changed into an isomeric  $\alpha \beta$  acid, as:



$\beta \gamma$  hydromuconic acid.



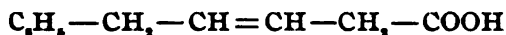
$\alpha \beta$  hydromuconic acid.

Even previous to this Fittig<sup>2</sup> had been led to the conclusion, that in the potassa-fusion of hydrosorbic acid a moving of the double union from the  $\beta \gamma$  to the  $\alpha \beta$  position must also take place, since the splitting, thereby occasioned, occurs at the  $\alpha \beta$  position with the production of butyric and acetic acids, still the hydrosorbic acid is unquestionably a  $\beta \gamma$  unsaturated acid, which, therefore, must split into two molecules of propionic acid.

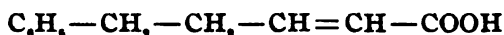
All these observations but favored the belief, that the shoving of the double union in the unsaturated acids towards the carboxyl group when boiled with caustic soda was a general one.

To prove the correctness of this point, Fittig began with his pupils, on a series of  $\beta \gamma$  unsaturated acids, and in all the researches as yet made, no exception has been found. Of the aromatic acids, aside from hydropiperic acid the following have been examined:

Phenyl  $\beta \gamma$  pentinic acid, which gives, according to T. Hoffmann, with boiling caustic soda, the isomeric phenyl  $\alpha \beta$  pentinic acid.



$\beta \gamma$

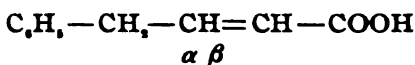
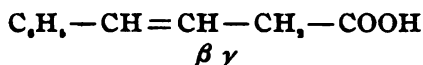


$\alpha \beta$

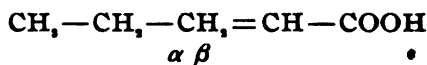
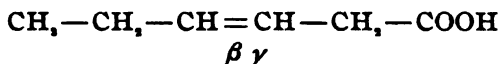
<sup>1</sup> Ibid., 256, 1.

<sup>2</sup> Ibid., 255, 13.

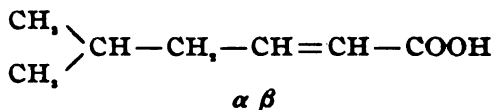
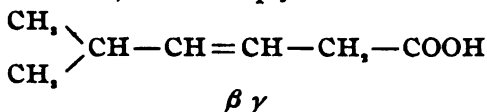
Phenylisocrotonic acid is changed, after Lüh, by a like treatment into benzylacrylic acid.



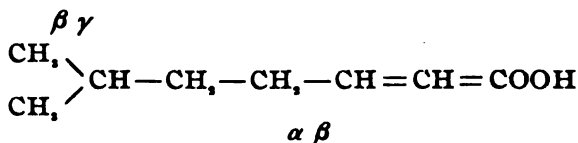
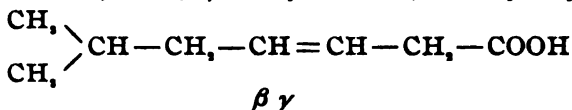
In the "fatty series" this change takes place regularly. Baker obtained from hydrosorbic acid by boiling with caustic soda  $\beta$  propylacrylic acid.



Feurer, from isoheptylic obtained isobutylacrylic acid.



Weill, from  $\beta \gamma$  isocetyl the  $\alpha \beta$  isoamylacrylic acid.



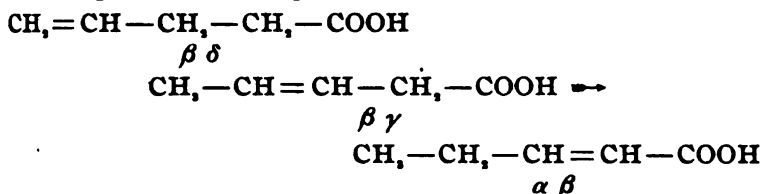
The present work was taken up with a view of extending these researches by including acids of the " $\gamma \delta$  series."

The supposition of Zincke and Kuester<sup>1</sup> that the  $\gamma \delta$  unsaturated acids would, when boiled with caustic soda, also allow of a displacement of their double bonds, can be given as one of the principal reasons for beginning the investigations.

If the supposition of Zincke and Kuester is correct, then the following, which they looked upon as very probable, would

<sup>1</sup> Ber. d. chem. Ges., 24, 909.

have been most interesting: that is, if the  $\gamma \delta$  acids should suffer their double bond to be moved, then it would be an easy matter to produce a  $\beta \gamma$  and in turn an  $\alpha \beta$  acid, for example, from allylacetic acid, ethylidenepropionic acid, and finally propylideneacetic acid should be obtained by boiling with caustic soda, according to the following:



The first part of this paper is taken up in the description of the results of the experiments, on two  $\gamma \delta$  acids, allylmalonic and allylacetic acids.

In the case of both of these acids, the following surprising results were obtained. On boiling with caustic soda no conversion into the corresponding  $\beta \gamma$  and  $\alpha \beta$  unsaturated acids could be detected. This passive behavior, of both of these representatives of the " $\gamma \delta$  series," is, therefore, the more remarkable, since from analogy, taken from the already observed inclination of terminal methylene radicals, to form methyl groups, as for instance, Faworsky<sup>1</sup> found in the unsaturated hydrocarbons, a complete change might be expected here. On the other hand Baeyer<sup>2</sup> has verified these exceptions to Faworsky's rule in the case of the hydrated phthalic acids.

Finally, if this difference to boiling caustic soda should be asserted in other  $\gamma \delta$  acids and become a general characteristic of this series, then through this means a sharp and decided distinguishing property has been discovered between the  $\gamma \delta$  and the  $\beta \gamma$  unsaturated acids, which, moreover, behave alike in the substitution of hydrobromic acid and the decomposition of the product, by means of water and alkalies (Messerschmidt<sup>3</sup>); as also in the substitution of bromine (Urban<sup>4</sup>); and in the treatment with potassium permanganate (Urban<sup>5</sup>).

The second part of this research is given to a description of the

<sup>1</sup> *J. prakt. Chem.*, 44, 212.

<sup>2</sup> *Ann. Chem.*, 269, 150.

<sup>3</sup> *Ibid.*, 208, 93.

<sup>4</sup> *Ibid.*, 268, 60.

<sup>5</sup> *Ibid.*, 268, 32.

results obtained in the treating with caustic soda the  $\beta \gamma$  acid corresponding to allylacetic acid, that is, ethyldenepropionic acid.

As a result it was found that this  $\beta \gamma$  unsaturated acid, like all the others, which have as yet been investigated, on boiling with caustic soda, allowed the double union to be shoved to the  $\alpha \beta$  position, with the formation of propyldeneacetic acid, formerly known, but until now only in the impure state.

Even from the first, investigators on the moving of the double bond of union, through the influence of boiling caustic soda, busied themselves with efforts to explain the mechanism of the reaction.

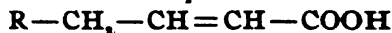
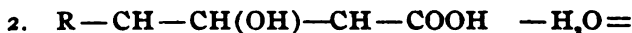
Based on analogous reactions Weinstein<sup>1</sup> suggested that by warming the  $\beta \gamma$  unsaturated acids with caustic soda the elements of water are taken up and an oxy acid formed, and this in turn, giving it up again, an  $\alpha \beta$  unsaturated acid results, as follows:



$\beta \gamma$  unsaturated.



$\beta$  oxy acid.



$\alpha \beta$  unsaturated.

This meanwhile purely hypothetical  $\beta$  oxy acid, forms, therefore, the intermediate step between the two isomeric unsaturated acids.

Although Weinstein himself could not isolate this oxy acid still it has been formed repeatedly since then, thus:

Luib obtained from phenylisocrotonic acid phenyl  $\beta$  oxybutyric acid  $C_6H_5-CH_2-CH(OH)-CH_2-COOH$ .

Hoffmann from phenyl  $\beta \gamma$  pentinic acid produced phenyl  $\beta$  oxyvalerianic acid.



However, just through Hoffmann's careful investigations, the idea that the  $\beta$  oxy acid was the middle link, in the change

<sup>1</sup> Ann. Chem., 227, 31.



from the  $\beta \gamma$  unsaturated, to the  $\alpha \beta$  acids was made somewhat doubtful.

He found for example that the  $\beta \gamma$  acid after six hours boiling with caustic soda gave fifty per cent. of  $\alpha \beta$  acid without any trace of  $\beta$  oxy acid, and that further, the formation of the oxy acid required a very long and protracted treatment with the alkali, and that finally, the  $\beta$  oxy acid can be most easily produced, by boiling the  $\alpha \beta$  acid with caustic soda. Briefly, his observations leave the impression as if the  $\beta$  oxy acid is not the intervening middle link between  $\beta \gamma$  and  $\alpha \beta$  acids, but is a secondary one to, and resulting from the  $\alpha \beta$  acid.

In the "fatty series," on the contrary, the reaction seems to follow the course of the above scheme of Weinstein even if it has certain restrictions.

Baker's work pointed to, and Feurer's observations made it certain, that the three acids which he examined  $\beta \gamma$  isoheptylic,  $\beta$  oxydimethylvalerianic, and  $\beta$  isobutylacrylic acids, when boiled with caustic soda, gave certain quantities of both of the others; the reaction does not, however, proceed smoothly in every sense of the term, but only to a certain limit, the  $\beta$  oxy acid always forming the intermediate product of the two unsaturated isomers.

These observations also cover the results described in the second part of this paper, they having been also noticed in the examination of the  $\beta$  oxy valerianic acid obtained from ethylidenepropionic acid.

#### PART I.

*On the behavior of allylmalonic and allylacetic acids when boiled with caustic soda solutions.*

#### PART II.

*On the behavior of ethylidenepropionic acid when boiled with caustic soda.*

*Contributions to the knowledge of propylideneacetic acid.*

#### PART I.

*Preparation of Allylmalonic Acid.*—The allylmalonic acid was produced according to Conrad and Bischoff,<sup>1</sup> from malonic acid, ethyl ester, and allyl iodide.

<sup>1</sup> *Ann. Chem.*, 204, 168.

The malonic acid ethyl ester was obtained from Claisen and Crismer's<sup>1</sup> modification of Conrad's<sup>2</sup> method; the allyl iodide in turn was prepared after Kannonikoff and Saytzev<sup>3</sup> and Wagner's<sup>4</sup> improved suggestions of Berthelot and Luca.<sup>5</sup>

Since the purity of the allylmalonic acid depends principally on the absolute purity of the allyl iodide, a few precautionary hints, which have recommended themselves during the course of preparation, may not be amiss here.

1. Some ignited sand was put into the retort, thereby overcoming, on the one hand, the danger of breaking the latter through the phosphorus or iodine becoming attached to the bottom of the retort, and on the other, the action of the phosphorus is rendered more uniform and regular.

2. The retort was filled to one-half or at least one-third of its capacity.

3. It is particularly desirable that the phosphorus react directly as it is brought into the retort and that the allyl iodide distill over at once; this is facilitated by covering the upper part of the bowl and beak of the retort with a cloth to guard against cooling.

If the allyl iodide is not carried over as soon as formed, then much isopropyl iodide is produced, which is only with the greatest difficulty separated from the allyl iodide. Through repeated careful fractional distillations a preparation boiling between 99° and 102° C. and possessed of only a light-red color, was obtained.

To prepare the allylmalonic acid ester, the allyl iodide was run as rapidly as possible into the well-cooled sodium malonic acid ester and the product obtained after two hours boiling, separated by shaking with ice-water, and fractioning without further drying. The fractions were collected at every 5° from 150° to 200°, and at every 2° from 200° to 235° C.

After repeated and successive fractioning the four portions from 218° to 226° were taken to be pure and so used.

The saponification of the ester, which Conrad and Bischoff<sup>6</sup> performed with potassium hydroxide was in this case accomplished with barium hydroxide, in which the four fractions from

<sup>1</sup> Ibid., 218, 131.

<sup>2</sup> Ibid., 204, 131.

<sup>3</sup> Ann. Chem., 185, 191.

<sup>4</sup> Ber. d. chem. Ges., 9, 1810.

<sup>5</sup> Ann. Chem., 204, 168.

<sup>6</sup> Ann. Chem., 204, 168.

218° to 226° were separately treated. After the saponification was complete, the contents of the flask were diluted with hot water and the excess of barium hydroxide removed by means of carbonic acid gas; it was now filtered, and the filtrate evaporated to obtain the crystalline barium allylmalonate in fractions, the several crystallizations of the original fractions being held separate, until the subsequent decomposition by means of hydrochloric acid proved them to be pure.

Thanks, to this careful and protracted process of fractioning, a white, almost perfectly pure acid was obtained, from which through the aid of the acid barium salt, an absolutely pure acid melting at 105° C. was prepared. The production of pure acid amounted to thirty-three per cent. of the theory.

*Boiling Allylmalonic Acid with Caustic Soda Solution.*—Two experiments were performed.

In the first one, ten grams of pure allylmalonic acid were boiled for twenty hours (in a copper flask, connected with a return condenser) with ten times the amount of caustic soda necessary for neutralization in a ten per cent. aqueous solution. Allowed to cool, the alkaline liquid was strongly acidified with sulphuric acid and shaken out with ether; after distilling off the ether a faintly yellow-colored oil remained behind, hardening to a white crystalline mass in a vacuum over sulphuric acid, and melting at 103° C. when crystallized out of benzene; after being purified by means of the acid barium salt the melting-point was raised to 105° C.; the substance was, therefore, pure and unaltered allylmalonic acid; it represented 9.591 grams or 95.9 per cent. of the acid originally used.

In the second test 7.3305 grams of allylmalonic acid were boiled in the same manner for twenty hours with a twenty per cent. solution of caustic soda representing ten times the necessary amount of alkali for neutralization; allowing to cool, acidifying, shaking out with ether, recrystallizing out of benzene, and purifying by means of the acid barium salt, 7.1345 grams of pure allylmalonic acid melting at 105° C. was recovered, corresponding to 97.3 per cent. of the amount used.

The loss of four and one-tenth per cent. in the first and two and seven-tenths per cent. in the second is explained by the fact

that it is impossible to recover the last portions of the acid from its solutions by means of ether.

The identity of the acid obtained, with allylmalonic acid, was not only proven by the melting-point, but also by other physical properties, as also by its deportment on distillation.

*Preparation of Allylacetic Acid.*—Zeidler<sup>1</sup> first obtained allylacetic acid from allylacetic acid ester and dry sodium ethylate, and stated its boiling-point to be 182° C. Conrad,<sup>2</sup> who got it by distilling allylmalonic acid, found the boiling-point to be 184° C.

According to Messerschmidt,<sup>3</sup> who used a modification of Zeidler's method, it boiled at 187° to 189° C.

Finally Marburg<sup>4</sup> studied the acid obtained by means of the Conrad as well as the Zeidler-Messerschmidt methods in both their physical and chemical properties and definitely settled the boiling-point at 186° to 187° C.

The allylacetic acid used in these researches was made after Conrad's process; it boiled constantly at 186° to 187° C. The production was about sixty-two per cent. of the theory.

*Boiling of Allylacetic Acid with Caustic Soda Solution.*—Ten grams of pure allylacetic acid boiling at 186° to 187° C. was boiled (in a copper flask connected with a return condenser) with ten times the amount of caustic soda necessary to neutralize it, in ten per cent. solution for twenty hours.

The cold contents of the flask were then strongly acidified with sulphuric acid and shaken out with ether, after distilling off the latter the residual acid was distilled with steam.

According to the statement given in the beginning of this paper one must consider the presence of  $\beta \gamma$ , and  $\alpha \beta$ , as well as of an oxy acid, and the use of steam was considered the better means of effecting their separation.

The distillation was continued until the distillate reacted neutral, the residual liquid in the distillation flask being then shaken out with ether; by this latter process nothing could be extracted; no oxy acid had, therefore, been formed.

The aqueous distillate was neutralized with barium carbonate

<sup>1</sup> *Ann. Chem.*, 187, 4.

<sup>2</sup> *Ibid.*, 204, 170.

<sup>3</sup> *Ibid.*, 208, 93.

<sup>4</sup> *Dissertation*, Strassburg, 1887.

in the cold, boiled, filtered, and evaporated to dryness; in this manner 15.85 grams of barium salt dried at  $100^{\circ}$  was obtained. The finely powdered salt was repeatedly extracted with hot absolute alcohol, thereby one and a half grams dissolved, remaining as an amorphous yellow-colored transparent mass, upon distilling off the alcohol. Redissolved in alcohol and allowed to evaporate in a desiccator it was again deposited amorphous. This experiment gave, therefore, 90.5 per cent. of barium salt insoluble in alcohol.

In order to obtain a larger amount of the soluble salt a second trial was begun under the same conditions as the first with ten grams of allylacetic acid; it gave 16.52 grams of dry barium salt of which one gram was soluble in hot alcohol leaving ninety-four per cent. undissolved. The two portions of insoluble barium salt were mixed, and a careful fractional crystallization begun. This process allowed of the eventual separation of the  $\beta \gamma$  and  $\alpha \beta$  acids from the barium allylacetate. To this end the salt was dissolved in the least possible amount of hot water, filtered, evaporated to a pellicle, and allowed to crystallize.

The first crystals obtained were flat and lanceolate prisms, later flat curved needles and leaves were shot out; an easily soluble salt could, however, not be detected.

The difference in appearance of the crystals would not necessarily point to the presence of different salts, since, on the one hand, pure barium allylacetate separates out in entirely different forms according as it crystallizes out more rapidly or slowly, and on the other hand, the last fractions could, when dissolved in water, adding alcohol until precipitation began, warming and then allowing to cool slowly, be obtained in small needle-shaped crystals of exactly the same appearance.

To examine the acid the several crystallizations together with their mother-liquors were mixed, the alcohol distilled off, and the organic acid set free and removed by successive treatments with hydrochloric acid and ether, the ethereal solution shaken with calcium chloride, filtered, and distilled from a small flask, the principal portion passed over from  $186^{\circ}$  to  $187^{\circ}$  C., a higher boiling fraction not occurring.

Because the barium salt had lost considerable in weight in

the successive evaporations (due to a slight decomposition) a third trial of boiling the allylacetic acid with caustic soda was made, in order to exclude any doubt of its conversion into  $\beta\gamma$  or  $\alpha\beta$  acid.

13.65 grams of allylacetic acid boiling at  $186^{\circ}$  to  $187^{\circ}$  C. and which had been recovered from former trials, were boiled with twenty per cent. sodium hydroxide for twenty-two hours, in the same manner as the others had been; also here the ether extract was entirely volatile, leaving no trace of an oxy acid.

The aqueous acid distillate was made slightly alkaline with sodium carbonate, evaporated to dryness, the sodium salt so obtained decomposed with sulphuric acid and extracted with ether. The ethereal extract was dried and gave 11.96 grams of an acid boiling at  $186^{\circ}$  to  $187^{\circ}$  C.; portions of a higher boiling-point were not present.

To more closely characterize the distillate 2.96 grams of the fraction boiling at  $186^{\circ}$  to  $187^{\circ}$  C., were subjected to the well-known "Lactone Reaction." For this purpose the acid was mixed with five times its weight of dilute sulphuric acid (one volume concentrated sulphuric acid and one volume water) in a small flask and heated just to boiling for fifteen minutes with constant agitation. The organic acid, which at first swam on the surface of the mixture, soon dissolved with a yellow coloration of the liquid; the contents of the flask was diluted with an equal volume of water and boiled for fifteen minutes, then cooled and extracted with ether.

The ethereal extract was dissolved in a little water, made slightly alkaline with sodium carbonate and at once shaken out with ether, a yellow-colored neutral liquid resulting, which, after drying, boiled constantly at  $206^{\circ}$  C., proving it to be pure valerolactone produced from the unaltered allylacetic acid.

The alkaline solution freed from lactone was, after removing the ether, acidified with sulphuric acid and distilled with steam; the distillate after neutralizing with calcium carbonate, filtering, and evaporating to dryness gave 0.1352 gram of a gray residue equivalent to 4.57 per cent. of the acid used.

From these three trials one can certainly conclude that by boiling allylacetic acid with caustic soda, neither propylidene

acetic acid, nor ethylidenepropionic acid, nor an oxy acid is formed in any quantity, which can be detected.

If a change does at all occur it is almost imperceptible. The small quantities of a barium salt soluble in alcohol were not sufficient to settle the question, whether it was the salt of the  $\alpha$   $\beta$  acid.

## PART II.

The ethylidenepropionic acid,  $\text{CH}_3\text{—CH=CH—CH}_2\text{—COOH}$  was prepared according to Fraenkel<sup>1</sup> by the distillation of methylparaconic acid.

*Preparation of Methylparaconic Acid.*—Methylparaconic acid was first made by Gantter<sup>2</sup> from acetosuccinic acid ester, by reducing with sodium amalgam and described under the name of ethylidene hydroxysuccinic acid. Fraenkel,<sup>3</sup> however, was the first one who obtained it pure; he prepared it by the condensation of acetaldehyde with sodium succinate; he also described it more closely.

The acid used in the present research was prepared according to Gantter's method, and since the preparation is somewhat difficult it may not be amiss to give it more than a casual description here.

1. Monochloracetic acid ester, was obtained after the Conrad<sup>4</sup> process; it gave a yield of eighty-five per cent. of the theoretical amount.

2. The acetosuccinic acid ester, was prepared according to Conrad's<sup>5</sup> process, which by fractioning under reduced pressure gave upwards of sixty per cent. of the theory.

In the acetosuccinic acid ester synthesis, it is of advantage to add the acetic acid ester, as well as the monochloracetic acid ester as rapidly as possible through a stoppered funnel into a flask containing the sodium ethylate and connected with a return condenser; by so doing the violent bumping of the contents of the flask is prevented; this can only otherwise be accomplished by filtering off the sodium chloride, which separates out in the reaction.

After the two esters have been brought together, the contents

<sup>1</sup> *Ann. Chem.*, 255, 24.

<sup>2</sup> Dissertation, Wuerzburg, 1878.

<sup>3</sup> *Ibid*, 255, 18.

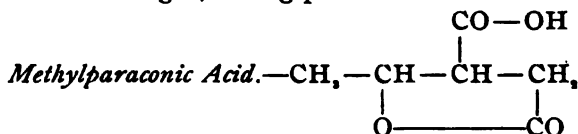
<sup>4</sup> *Ibid*, 188, 218.

<sup>5</sup> *Ann. Chem.*, 188, 218.

of the flask are kept boiling on the water-bath for two hours, allowed to cool, mixed with ice-water, and extracted with ether; a reddish-brown crude ester is obtained, which, after being shaken with small portions of water, is subjected to fractional distillation. Drying by the use of calcium chloride is not to be recommended, since the salt dissolves, and when distilled, causes a decomposition of the ester, as Gottstein<sup>1</sup> and Young<sup>2</sup> have also observed in similar esters.

To free the crude ester of ether, alcohol, water, unaltered acetic acid ester, and monochloroacetic acid ester, it was heated to 200° C. That portion, which did not distill off at this temperature, was then fractioned in a rarefied atmosphere under fifty mm. pressure and this repeated three times, gave an ester boiling at 180° to 183° C.

This was accepted as pure acetosuccinic acid ester; it presented a colorless pleasant smelling liquid almost as thick as glycerol. By fractioning under the ordinary pressure it was never found possible to obtain an ester as colorless, nor boiling as constantly, and notwithstanding the statements of Conrad<sup>3</sup> it is the author's opinion that it can not be distilled under ordinary pressure even when perfectly pure, without a decomposition more or less slight, taking place.



Pure acetosuccinic acid ester, in portions of twenty-five grams each, was mixed with a like quantity of absolute alcohol, and water added to a turbidity, then four per cent. sodium amalgam was added, the vessel being frequently agitated. At the beginning the sodium amalgam melted in a short time without any perceptible evolution of gas; when the reaction diminished in consequence of the concentration of the liquid more water was added until turbidity again appeared and the reaction renewed.

The mercury resulting from the decomposition of the amalgam was taken out from time to time with a pipette, washed with water, and the wash-water added to the original reducing fluid.

<sup>1</sup> Ibid, 216, 31-36.<sup>2</sup> Ibid, 216, 43.<sup>3</sup> Ann. Chem., 188, 218.



The latter was, during the process of reduction, neutralized with dilute sulphuric acid to prevent the accumulation of a large excess of alkali. The entire process was continued until three times the theoretical amount of sodium amalgam had been added.

It is necessary in the reduction to observe that the solution does not become too warm (for this reason it may be well to set the vessel containing it, into ice-water at the beginning), also that it does not become too alkaline, otherwise a splitting of the acetosuccinic acid ester can easily occur, which, according to Wislicenus,<sup>1</sup> can follow in two directions.

When the sodium amalgam had ceased to act the liquid was, after removing and washing the mercury, exactly neutralized with dilute sulphuric acid, filtered, evaporated to a small volume, and allowed to crystallize, the mother-liquor drained off from the crystals of sodium sulphate, acidulated with sulphuric acid, and extracted with ether; the ethereal residue at first a yellow oil, soon becomes a solid mass when placed in a vacuum over sulphuric acid. This solid mass relieved of the oily matters by suction with a filter pump and pressure between bibulous paper gave, when broken into small pieces and kept over sulphuric acid in a vacuum, a perfectly dry white powder; this was the desired methylparaconic acid.

It was crystallized out of benzene in the following manner: A flask containing the powdered acid and some benzene, and fitted with a perforated cork, through which passed a long glass tube, was heated by plunging it into boiling water, it being constantly agitated, so as to bring the now melted underlying acid into intimate contact with the supernatant solvent; allowed to settle, and the clear solution decanted (from the liquid and still undissolved acid) into flasks, which were at once stoppered and set aside to crystallize. To the still undissolved acid in the first flask more benzene was added and the same process continued until no more was dissolved.

If before being dissolved in the benzene the acid was perfectly dry and therefore free from all oily matters then it dissolves completely and crystallizes out in hard dry crystals; if, however,

<sup>1</sup> *Ibid.*, 190, 275.

the oil has not been entirely removed, then the acid separates out as a sticky mass; should this be the case then it must be freed from the solvent, the oil thoroughly removed by pressing between bibulous paper, drying, and again crystallizing out of benzene.

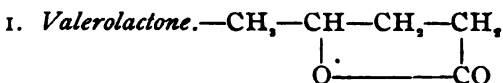
The production of pure acid was twenty per cent. of the theoretical.

*Preparation of Ethylidenepropionic Acid.*—The ethylidenepropionic acid was made according to Fraenkel.<sup>1</sup> Pure methylparaconic acid, in portions of fifteen grams each, was carefully heated in a small distillation flask; at first the acid melted to a colorless fluid, but took on a yellowish-red coloration as the operation advanced. When the temperature of the molten acid had reached 200° C. a slight evolution of carbon dioxide had begun and as the immersed thermometer indicated 240° to 260° C. the evolution of gas was a very regular one.

The thermometer bulb was now drawn up to the opening of the exit tube and the distillation continued to the end, the vapors passing over at 210° to 220° C. A slight carbonaceous residue representing nine-tenths per cent. of the acid used, alone remained behind.

The distillate, a yellowish oil of a strong empyreumatic odor contains:

1. Valerolactone.
2. Ethylidenepropionic acid.
3. Methylcitraconic acid.
4. Methylitaconic acid, and
5. Unaltered Methylparaconic acid.



The empyreumatic distillate, mixed with five times its volume of water, was made slightly alkaline with sodium carbonate in the cold, and rapidly extracted with ether; a reddish-yellow oil resulted, which, after removing the ether and water, could be easily characterized as valerolactone.

<sup>1</sup> *Ann. Chem.*, 255, 24.

2. *The Acids*.—The alkaline solution, from which the lactone had been extracted, was acidulated with sulphuric acid and completely extracted with ether; the acid mixture so obtained was distilled with steam until the distillate ceased to be acid. The slightly turbid distillate was made faintly alkaline with barium hydroxide, treated with carbonic acid gas, boiled, and filtered; in this manner a solution of barium ethylidenepropionate and methylcitrate was obtained, which can be separated by fractional crystallization.

The acid residue left in the distillation flask after distilling with steam, was evaporated to a small bulk, when it solidified to a yellow crystalline mass on being placed over sulphuric acid in a vacuum.

By treating this mass with cold chloroform the unaltered methylparaconic acid was easily extracted, while the methylitaconic acid, which was present only in small quantities, remained undissolved as a powder; the latter, like the methylcitric acid, was not used further.

To separate the barium methylcitrate from the barium ethylidenepropionate, the solution containing both was simply evaporated when the barium methylcitrate difficultly soluble in the heat separated out; it was then filtered again, evaporated, and so continued until no more salt difficultly soluble in the heat, separated out. The mother-liquors deposited upon further evaporation, when cold, the barium ethylidenepropionate in the form of flat lanceolate prisms grouped together into stars. To remove every trace of barium methylcitrate, the barium ethylidenepropionate was recrystallized three times. It was then exactly decomposed with a weak solution of sodium sulphate, and thereby, after filtering and evaporating, sodium ethylidenepropionate obtained, in which form it was later mostly used.

200 grams of methylparaconic acid gave about forty-five grams, or twenty-two and one-half per cent. of ethylidenepropionic acid.

*Preparation of Propylideneacetic Acid*.—By the action of propionaldehyde on malonic acid Komnenos<sup>1</sup> obtained a monobasic unsaturated acid with five atoms of carbon, which he called pro-

<sup>1</sup> *Ann. Chem.*, 218, 166.

pylideneacetic acid. In the same manner Zincke and Kuester,<sup>1</sup> as well as Ott<sup>2</sup> and Vieffhaus,<sup>3</sup> prepared their propylideneacetic acid.

Zincke and Kuester<sup>4</sup> also obtained, in an entirely different manner, an acid which they recognized to be identical with Komnenos's propylideneacetic acid.

Starting with hexachlordiketo R hexane obtained from catechol, orthoamidophenol and chlorine they prepared successively tetrachlorocatechol or tetrachloramidophenol, and then pentachlorbutane carbon dioxide, and by treating the latter with sodium amalgam, procured their acid.

Fittig and Fraenkel,<sup>5</sup> however, suspected that the above acid of Zincke and Kuester was identical with ethylidenepropionic acid, obtained from methylparaconic acid; this supposition was, through the later researches of Zincke and Kuester,<sup>6</sup> made very probable, inasmuch as these investigators obtained small quantities of lactone by treating the bromhydric acid addition product of their acid with water, from which it would appear that the acid must be ethylidenepropionic acid or at least contain it as an impurity, since pure propylideneacetic acid can produce no lactone.

Such acids as have been prepared and described under the name of propylideneacetic acid are no homogeneous bodies. It was not until the writer, in July, 1892, procured the acid in its crystalline form by boiling ethylidenepropionic acid with caustic soda; and Mackenzie,<sup>7</sup> in February, 1893, secured it after the method of Komnenos that pure propylideneacetic acid had been made and characterized.

*Boiling of Ethylidenepropionic Acid with Sodium Hydroxide.*—Sodium ethylidenepropionate, in portions of ten grams each, was boiled with thirty-three grams of sodium hydroxide dissolved in 295 grams of water for fifteen hours in a copper flask connected with a return condenser. The cold alkaline solution was now acidulated with ether, the ethereal extract distilled with steam until the distillate came over perfectly neutral; the milky acid

<sup>1</sup> *Ber. d. chem. Ges.*, 22, 494. *Ibid.*, 23, 818. *Ibid.*, 24, 909.

<sup>2</sup> *Ibid.*, 24, 2,600.

<sup>3</sup> *Ibid.*, 26, 915.

<sup>4</sup> *Ibid.*, 21, 2,719.

<sup>5</sup> *Ibid.*, 255, 33.

<sup>6</sup> *Ber. d. chem. Ges.*, 24, 909.

<sup>7</sup> Dissertation, Strassburg, 1894.

distillate was neutralized with barium carbonate in the cold, filtered, and evaporated to dryness.

From the liquid remaining in the distillation flask the  $\beta$  oxyvalerianic acid was obtained (see  $\beta$  oxyvalerianic acid).

To separate the ethylidenepropionic acid and expected propylideneacetic acids, the dry barium salt was repeatedly extracted with hot alcohol and filtered hot each time; the barium salt remaining undissolved was perfectly white and proved to be unaltered barium ethylidenepropionate; it was through double decomposition with sodium sulphate changed to the sodium salt, in which form it was again boiled with caustic soda. In the alcohol another barium salt had been dissolved; on distilling off the solvent a light yellow-colored, amorphous varnish-like mass was left behind; this was supposed to be the barium salt of the newly formed  $\alpha \beta$  acid.

To remove every trace of  $\beta \gamma$  acid from it, the barium salt was decomposed with sodium sulphate forming the sodium salt, and this mixed with a quantity of dilute sulphuric acid (one volume concentrated sulphuric acid and one volume of water), corresponding to five times the amount of organic matter present, plus a sufficiency to neutralize the sodium of the sodium salt and heated in a flask almost to boiling, with constant agitation for fifteen minutes, then mixed with a like bulk of water and boiled for thirty minutes. Allowed to cool, the acid solution is extracted with ether, the ethereal extract again rapidly boiled with some water, and a few drops of dilute sulphuric acid to again change into lactone any oxy acid, which may have been formed, rapidly cooled off, sodium carbonate added to an alkaline reaction, and the lactone at once shaken out with ether. The alkaline solution free from lactone was again acidified, extracted with ether, and the ethereal residue distilled with steam, the acid distillate neutralized with sodium carbonate anew, and the sodium salt obtained, again treated with sulphuric acid as above. The entire operation was repeated until no more lactone was found; this was accomplished after repeating it two or three times, when every trace of  $\beta \gamma$  acid had surely been removed.

Propylideneacetic acid:  $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{COOH}$ .

After no more lactone could be detected in shaking the alkali-

line liquid after boiling with sulphuric acid, the solution was acidified and distilled with steam, and from the acid distillate the sodium or calcium salt of the  $\alpha\beta$  acid produced. On decomposing the sodium salt with sulphuric acid, or the calcium salt with hydrochloric acid in a narrow tube, the pure  $\alpha\beta$  acid was obtained as an almost colorless oily layer; it was drawn off, the last portions extracted with ether, and the ethereal solutions dried by means of dried sodium sulphate or calcium chloride, filtered, and the ether evaporated, leaving a colorless oil, which congeals in a freezing mixture at once and remaining solid indefinitely in ice-water, since it melts at  $7\frac{1}{4}^{\circ}$  to  $8\frac{1}{4}^{\circ}$  C.

In cold winter weather it is extremely easy to obtain the acid perfectly pure and of the correct melting point.

The acid from the ethereal extract is poured into a watch-glass and placed in a desiccator at a low temperature; it then solidifies in flat rhombohedral tables or leaves, which can, with the aid of a cold platinum wire, be brought upon a piece of filter paper, to there give up the last traces of moisture, remaining behind as flat, glistening crystals. The acid is therefore the  $\alpha\beta$  acid, corresponding to the ethylidenepropionic acid; its melting-point, compared with a specimen of the acid subsequently prepared, after the method of Komnenos,<sup>1</sup> which was purified and crystallized in a like manner, gave the following results.

A specimen of each was placed on the bulb of the same thermometer and plunged into a freezing mixture for a minute and then into cold water, the temperature of which was gradually raised.

At  $6\frac{1}{2}^{\circ}$  C. they both remained solid.

At  $7^{\circ}$  C. likewise so.

At  $7\frac{1}{4}^{\circ}$  C. both samples began to melt slightly.

At  $7\frac{1}{2}^{\circ}$  C. both were about half melted.

At  $8^{\circ}$  C. only a small quantity of each still remained solid.

At  $8\frac{1}{4}^{\circ}$  C. both were completely melted.

The melting-point determinations were made by placing the acid in thin-walled melting-point tubes two mm. in diameter, and closed at both ends; this allowed of a repetition of the esti-

<sup>1</sup> *Ann. Chem.*, 218, 166.

mations without any danger of loss by evaporation or inaccuracy from the absorption of water.

During some recent work on propylideneacetic acid by the Komnenos' process, Mackenzie<sup>1</sup> found the melting-point to be  $9\frac{1}{4}^{\circ}$ – $10\frac{1}{4}^{\circ}$  C.

It is much more difficult to obtain the solid acid of a constant melting-point in summer; to this end the following method was used: The acid freed, as much as possible, from ether and water, contained in a small flask held horizontally, was moved backwards and forwards through a water-bath of  $65^{\circ}$  C., in order to remove the last traces of ether. The flask was then closed with a stopper and calcium chloride tube, and plunged into a freezing mixture of ice and salt, in such a manner that the acid congeals on one side of the flask; the flask was now placed upright in a vessel of ice-water for an hour; the mother-liquor draining out was poured off; finally the crystalline cake was itself slightly warmed, so that the last low melting portions of the acid percolated out what remained congealed in a freezing mixture completely and did not remelt in ice-water.

Pure propylideneacetic acid becomes solid at  $0^{\circ}$  C.; if the melted acid be placed in ice-water, it solidifies in half an hour. If a crystal of the acid be dropped in, it congeals at once. The smallest quantities of water or ether have a decided effect on its melting-point.

At the ordinary temperature pure propylideneacetic acid is a mobile colorless liquid with a faint, pleasant odor of acetic acid. It is so volatile, that even at  $45^{\circ}$  C. it passes over with the ether vapors, and in summer a considerable loss is not to be prevented when working with this substance.

About sixty per cent. of the ethylidenepropionic acid is converted into propylideneacetic acid by boiling with caustic soda. For analysis the acid melting at  $7\frac{1}{4}^{\circ}$  to  $8\frac{1}{4}^{\circ}$  C. was used.

1. 0.2716 gram acid gave 0.1915 gram  $H_2O$ , and 0.595 gram

2. 0.2965 gram acid gave 0.2125 gram  $H_2O$ , and 0.6508 gram

<sup>1</sup> Dissertation, Straassburg, 1894.

	Calculated for $C_5H_5O_4$	1.	Found.	2.
C .....	60.00	59.75 per cent.		59.86 per cent.
H .....	8.00	7.84	"	7.96 "

*Salts of Propylideneacetic Acid.*—Barium Salt. The barium salt of propylideneacetic acid is very characteristic; it was prepared by neutralizing propylideneacetic acid with barium carbonate suspended in water; the neutral solution was boiled, filtered, and evaporated to a pellicle; after cooling, the pellicle was removed from the surface of the solution and the liquid placed in an ice-chest (for when allowed to evaporate at the ordinary temperature a sticky mass only separates out) to undergo a very slow evaporation. After some weeks the salt is deposited in needles grouped to rosettes; these were washed and subjected to analysis.

The salt contains considerable water of crystallization, but effloresces easily, becoming anhydrous in a desiccator over sulphuric acid.

1. The salt pressed between filter paper and allowed to remain in an ice-chest on a piece of filter paper over night, was on the following morning weighed into an open crucible, and allowed to remain in a desiccator to constant weight.

0.2102 gram lost 0.0170 gram  $H_2O$  or 8.10 per cent.

2. The pressed salt was, after remaining for fifteen minutes on a piece of filter paper in the ice-chest, weighed into an open crucible and allowed to remain to constant weight in a desiccator.

0.6470 gram lost 0.1028 gram  $H_2O$  or 15.88 per cent.

3. The pressed salt was placed for twenty-five minutes in the air at  $14^\circ C.$  and then treated as above.

0.2493 gram lost 0.0203 gram  $H_2O$  or 8.14 per cent.

4. 0.1932 gram of the salt dried in a desiccator gave 0.1335 gram  $BaSO_4$ , 0.0785 gram Ba.

Calculated for $(C_5H_5O_4)_2 Ba$ .	Found.
40.89 per cent. Ba.	40.63 per cent. Ba.

It follows from these determinations that because of the disposition of this salt to effloresce, it is impossible to make an exact estimation of the water; the difference in amount seems to depend on the temperature at which the crystallization takes place.



It was found impossible to examine the crystals optically; one can only see that they are tables with end faces, but to which system they belong can not be said.

To observe the deportment of the crystallized salt at a higher temperature, a portion which had crystallized out in the ice-chest was placed together with its mother-liquor in a stoppered vessel and allowed to remain several days at a temperature of 20° C.; a part of the crystals were thereby dissolved; the other portion, however, remained crystalline and did not become sticky.

**Calcium Salt.** The calcium salt was made by neutralizing an aqueous solution of the acid with calcium carbonate in the cold; the solution boiled, filtered, and evaporated to a pellicle; on cooling, the salt crystallized out in moderately long, flat, glistening prisms; they were collected on a platinum cone, washed, dried, and laid on filter paper for twelve hours at 6° C. The salt gives off all its water of crystallization in a desiccator.

0.4155 gram gave 0.0985 gram  $H_2O$ .

Calculated for  $(C_5H_7O_2)_2, Ca + 4H_2O$ .

23.22 per cent.  $H_2O$ .

Found.

23.71 per cent.

0.2263 gram of salt dried at 100° C. gave 0.1298 gram  $CaSO_4$ .

Calculated for  $(C_5H_7O_2)_2, Ca$ .

16.81 per cent.  $Ca$ .

Found.

16.87 per cent.  $Ca$ .

The calcium salt crystallizes much easier than the barium salt, since it can be obtained at a temperature of 16° C. in nice prisms, while the barium salt always becomes sticky at this temperature. Calcium propylideneacetate like the barium salt is easily soluble in water and alcohol.

*Propylideneacetic acid dibromide.*

$\alpha$   $\beta$  dibromvalerianic acid.

$\alpha$   $\beta$  pentinic acid dibromide.

$CH_3-CH_2-CHBr-CHBr-COOH$ .

To further characterize the acid, the bromine and bromhydric acid addition products were made.

To prepare the dibromide, the vessels and reagents used were carefully dried.

The acid was dissolved in a little carbon disulphide and then with exclusion of air the calculated amount of bromine in a ten per cent. carbon disulphide solution was added through a drop-

per funnel-tube. A violent reaction was not noticed even at the commencement, the decolorization being slow and incomplete. The experiment was conducted in diffused daylight.

After a small excess of bromine had been added, the whole was cooled off and allowed to remain quiet for twenty-four hours; the most of the carbon disulphide was then removed by aspirating a current of dry air through the bottle; the remaining solution was placed on a large watch-glass in a desiccator, and the disulphide entirely removed by frequent stirring with a glass rod. The desiccator placed in a refrigerator soon caused the dibromide to crystallize out in large leaves.

After the disulphide had been completely removed by alternate stirring, and evacuation of the desiccator, the solid dibromide was dissolved in the least possible quantity of petroleum ether, and the solution allowed to stand in a corked test-tube for several hours. Here the dibromide was deposited in rosettes of flat prisms on the sides of the tube. The mother-liquor was rapidly decanted and the crystals washed two or three times with cold ( $0^{\circ}$  C.) petroleum ether, and again crystallized out of the latter, when the preparation was considered pure.

The dibromide seems not adapted for crystallographic study; the crystallization is probably monosymmetric; it melts without coloration at  $56^{\circ}$  C.; it is very soluble in carbon disulphide and benzene; in petroleum ether it is easily soluble.

0.2040 gram of the dibromide dried in a vacuum gave 0.2957 gram of AgBr = 0.1258 gram Br.

Calculated for  $C_5H_8Br_2O_2$ .

61.54 per cent. Br.

Found.

61.68 per cent. Br.

$\beta$  Bromvalerianic acid.  $CH_3-CH_2-CHBr-CH_2-COOH$ .

The hydrobromic acid addition product of propylideneacetic acid was prepared as follows: To one volume of the pure acid contained in a small cylinder having a well-ground stopper, one and a half volumes of hydrobromic acid saturated at  $0^{\circ}$  C. were added; on shaking, a clear solution resulted; it was allowed to remain quietly for twenty-four hours at the ordinary temperature; the monobromide had now risen to the surface of the hydrobromic acid as a light brown-colored layer. The cylinder was now vigorously shaken from time to time, to bring any

unaltered propylideneacetic acid which might be dissolved in the monobromide, into intimate contact with the hydrobromic acid. After this occasional shaking had been continued four or five days, the contents of the cylinder formed two distinct layers; the reaction was ended and all the propylideneacetic acid had been quantitatively changed into  $\beta$  bromvalerianic acid. The cylinder, still stoppered, was now placed in ice-water to cause the new acid to solidify, this, however, did not occur. It was then placed in a freezing mixture of ice and salt, and on agitating slightly, the monobromide at once congealed to a mass of fine needles lying on the surface of the hydrobromic acid. The cylinder stood for fifteen hours at a temperature of  $15^{\circ}\text{C}.$ ; then the crystalline cake was broken through with a glass rod, distributed through the hydrobromic acid, and brought into a platinum cone where it was allowed to dry, being washed with small successive portions of ice-water, in order to remove the greater part of the mineral acid. The contents of the cone were now brought upon a watch-glass and placed in a vacuum over sulphuric acid and potassium hydroxide; a dry sandy-white substance resulted, which was powdered and recrystallized out of petroleum ether. So produced, the  $\beta$  bromvalerianic acid is, after drying, perfectly pure, as the analysis proves.

0.233 gram of the substance dried in a vacuum gave 0.2410 gram AgBr.

Calculated for  $\text{C}_5\text{H}_9\text{BrO}_2$ .

44.20 per cent. Br.

Found.

44.20 per cent. Br.

$\beta$  bromvalerianic acid melts at  $59^{\circ}$  to  $60^{\circ}\text{C}.$ , the melting-point not altering in the least by repeated determinations on the same sample.

It dissolves readily in ether, chloroform, carbon disulphide, less easily in benzene and petroleum ether, and is almost insoluble in water of  $0^{\circ}\text{C}.$

If the cold, saturated solution of the monobromide in petroleum ether be allowed to evaporate spontaneously it crystallizes out in beautiful, colorless, eight-sided prisms.

The crystals set up after Naumann's system give the following crystallographic measurements:

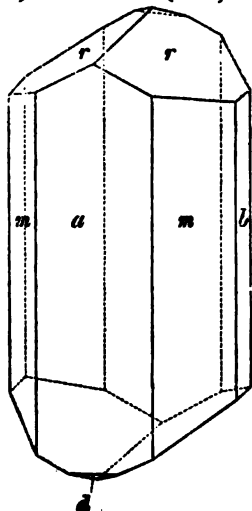
$\beta$  BROMVALERIANIC ACID.

Crystal system : Monosymmetric.

$$a : b : c = 1.4688 : 1 : 0.4900$$

$$\beta = 79^{\circ} 58' 45''$$

Observed forms:  $m = \{110\} \infty P$ ,  $a = \{100\} \infty \bar{P}\infty$ ,  $b = \{010\} \infty \bar{P}\infty$ ,  
 $r = \{011\} \bar{P}\infty$ ,  $d = \{\bar{1}01\} + \bar{P}\infty$ ,  $e = \{101\} - P\infty$ .



The crystals are mostly two to five mm. long by one to two mm. wide, and possess a valerianic acid-like odor.

Some crystals are minus  $[\bar{1}01] + \bar{P}\infty$ , as also  $[100] \infty \bar{P}\infty$ , while  $[10\bar{1}] - \bar{P}\infty$  was only observed once.

The faces were almost always smooth and polished, giving excellent reflexes.

The following angles were measured and calculated:

	Measured.	Calculated.
$r : r = (011) : (0\bar{1}1) =$	$51^{\circ} 31'$	.....
$a : m = (100) : (110) =$	$55^{\circ} 20' 30''$	.....
$r : m = (011) : (\bar{1}00) =$	$99^{\circ} 1'$	.....
$m : m = (110) : (1\bar{1}0) =$	$110^{\circ} 43'$	$110^{\circ} 41'$
$m : b = (110) : (010) =$	$34^{\circ} 47'$	$34^{\circ} 39' 30''$
$r : b = (011) : (010) =$	$64^{\circ} 6'$	$64^{\circ} 14' 30''$
$a : b = (100) : (010) =$	$89^{\circ} 58'$	$90^{\circ}$
$a : d = (100) : (\bar{1}01) =$	$99^{\circ} 2'$	$99^{\circ} 12'$

	Measured.	Calculated.
$r : m = (oII) : (\bar{II}O) =$	$74^{\circ} 2'$	$74^{\circ} 26'$
$a : e = (IOO) : (IOI) =$	$61^{\circ} 59'$	$62^{\circ} 44'$
$r : d = (IOI) : (\bar{IO}I) =$	$36^{\circ} 33'$	$36^{\circ} 29'$
$r : m = (oII) : (\bar{II}O) =$	$63^{\circ} 33'$	$63^{\circ} 28'$
$r : d = (oII) : (\bar{IO}I) =$	$31^{\circ} 8'$	$31^{\circ} 45'$
$d : m = (\bar{IO}I) : (\bar{IO}O) =$	$80^{\circ} 11'$	$80^{\circ} 48'$

A cleavage could not be found. The plane of the optical axes stands at right angles to the klinopinacoid and is only slightly inclined towards the orthopinacoid.

Obtuse bisectrix = b axis.

$\beta$  Oxyvalerianic acid,  $\text{CH}_3\text{—CH}_2\text{—CH(OH)—CH}_2\text{—COOH}$ .

The acid mixture from the treatment of ethylidenepropionic with caustic soda was not completely volatile with steam.

The residue left in the distillation flask, after the ethylidene-propionic and propylideneacetic acid had been driven over, had a strong acid reaction and gave up a yellow oil when shaken with ether. It was purified by dissolving in ether and precipitating with petroleum ether as a thick colorless liquid. This syrup could not be solidified either by allowing it to remain in a desiccator or at a temperature of  $18^{\circ}\text{C}$ . for several hours, aided by frequent stirring with a platinum wire. A portion of the acid, which had been prepared from the perfectly pure barium salt, was dried in a desiccator to constant weight; it then presented an absolutely colorless liquid, which, when put into a narrow test-tube and placed in a freezing mixture, would not become solid with frequent stirring by means of a platinum wire. At best it remained a colorless molasses-like liquid, although the barium salt from which it was obtained as well as the acid itself, as far as purity is concerned, left nothing to be desired as the analyses show.

0.2745 gram obtained from the pure barium salt contained in a platinum boat and dried in a desiccator gave 0.2073 gram  $\text{H}_2\text{O} + 0.5105$  gram  $\text{CO}_2$ .

	Calculated for $\text{C}_5\text{H}_8\text{O}_3$ .	Found.
C .....	50.85 per cent..	50.72 per cent.
H.....	8.47     "	8.39     "

$\beta$  oxyvalerianic acid is easily soluble in cold water, ether, benzene, and in chloroform; in carbon disulphide and petroleum ether it is insoluble.

From forty-five grams of ethylidenepropionic acid, which was boiled with caustic soda, 16.5 grams or thirty-six per cent. of  $\beta$  oxyvalerianic acid was produced.

*Salts of  $\beta$  Oxyvalerianic Acid.*—Calcium Salt. The still yellow-colored acid was diluted with water and heated on the water-bath until the mixture reacted neutral; it was then filtered and the yellow-colored filtrate decolorized with animal charcoal; the filtered solution was now evaporated until a pellicle formed on the surface and was then allowed to cool; the pellicle was dissolved and after remaining at the ordinary temperature for some time there was deposited on the bottom of the vessel a collection of white opaque warts of porcelain-like appearance, which, when powdered and dried in the air, was analyzed.

1. 0.43 gram of air-dried salt lost 0.0263 gram $H_2O$ at $175^\circ C$ .	
Calculated for $(C_5H_7O_3)_2 Ca + H_2O$ .	Found.
6.16 per cent. $H_2O$ .	6.12 per cent.
2. 0.1889 gram anhydrous salt gave 0.0915 gram $CaSO_4$ .	
Calculated for $(C_5H_7O_3)_2 Ca$ .	Found.
14.59 per cent. $Ca$ .	14.30 per cent.

The salt retains its water of crystallization very tenaciously and gives it up when heated for some time at  $175^\circ C$ . At  $180^\circ C$ . it begins to melt and acquire a yellow tint, whereby it loses considerable in weight and at  $200^\circ C$ . a yellow transparent molten mass filled with bubbles results, with an increase in the amount of decomposition, which began at  $180^\circ C$ . The salt is quite soluble in water and insoluble in alcohol. Still the aqueous solution, to which three volumes of absolute alcohol has been added, remains perfectly clear at first, only becoming cloudy after the lapse of some hours, and after a longer period the salt is deposited as a sandy indistinctly crystalline mass.

Treated with alcohol on a slide and examined under the microscope the following was observed:

The precipitate consists of small, mostly irregularly formed, double refracting leaves, stretched at times in one direction, and which present an oblique obliteration of light, parallel to this principal direction of development. Because of this oblique obliteration the crystals probably belong to the monoclinic system.

Barium Salt.—The barium salt was prepared in exactly the same manner as the preceding, by warm neutralization of

barium carbonate; the solution evaporated to a pellicle, was allowed to cool, the pellicle not dissolving; after about an hour it became cloudy, and deposited small, fine needles, which gradually accumulated on the bottom of the beaker as a sandy crystalline mass.

This crystalline mass treated with alcohol and examined under the microscope, showed a colorless, strongly double refracting homogeneous number of crystals, grouped to a half ball; they were tables of rhombic or right angular form, with an oblique obliteration and were, therefore, probably monoclinic.

0.1983 gram of the air-dried salt lost 0.0093 gram  $H_2O$  at  $105^\circ C.$  and gave 0.1193 gram  $BaSO_4$ .

Calculated for $(C_5H_7O_2)_2 Ba + H_2O$ .		Found.
$H_2O$ .....	4.63 per cent.	4.67 per cent.
Ba .....	35.22 "	35.36 "

At  $105^\circ C.$  the salt melts without decomposition to a colorless transparent mass; even, on the water-bath, when covered with a little water a thick syrup results. It is insoluble in alcohol.

**Silver Salt.**—The silver salt was obtained by the double decomposition of a warm concentrated solution of the calcium salt with silver nitrate, as slightly violet-colored crystals or a powder according as it separated out rapidly or slowly. When recrystallized from hot water it is nearly white and is but little affected by light.

0.1037 gram of the salt dried at  $50^\circ$  to  $55^\circ C.$  gave in the combustion 0.0497 gram Ag.; 0.1018 gram  $CO_2$ ; and 0.0390 gram  $H_2O$ .

Calculated for $(C_5H_7O_2)_2 Ag$ .		Found.
Ag. ....	48.00 per cent.	47.93 per cent.
C .....	26.67 "	26.86 "
H.....	4.00 "	4.27 "

Microscopically the crystalline powder appeared to be fine, flat, at times, corroded needles, which had an oblique obliteration in their long direction.

**Boiling  $\beta$  Oxyvalerianic Acid with Sodium Hydroxide.**—For this very interesting experiment 6.240 grams of calcium  $\beta$  oxyvalerianate (representing five grams of acid) was used; through double decomposition with sodium carbonate sodium  $\beta$  oxyvalerianate was formed and this boiled for thirty hours in a copper flask connected with a return condenser and containing 17.1 grams, of sodium hydroxide in 154 grams of water.

After cooling, the solution was acidified with sulphuric acid and extracted with ether. The ethereal residue rapidly boiled with water and a few drops of dilute sulphuric acid, to change any  $\gamma$  oxy acid present (which could have originated from the  $\beta$  oxy acid with ethylidenepropionic acid and valerolactone as intermediate steps) into lactone, was then made slightly alkaline with sodium carbonate, and shaken out with ether; nothing was taken up by the latter, consequently, the presence of  $\gamma$  oxy acid must be excluded.

The alkaline solution, after the ether had been removed, was acidulated with sulphuric acid and distilled with steam until the distillate passed over the neutral. The unaltered  $\beta$  oxy acid remained behind in the distillation flask, which, when shaken with ether, allowed of its removal from the contents of the same; it was converted into the calcium salt, which amounted to three and four-tenths grams or more than one-half of the acid originally employed.

The acid distillate was neutralized with barium carbonate, but since the barium salts thus obtained do not allow a good separation with alcohol, they were converted into the sodium salts through the aid of sodium sulphate, and now the  $\beta \gamma$  acid converted into lactone by boiling with sulphuric acid, made alkaline with soda solution, the lactone was shaken out with ether, and characterized by boiling with barium hydroxide for thirty minutes, thus converting it into the barium salt of  $\gamma$  oxyvalerianic acid. After precipitating the excess of barium with carbon dioxide in the heat, the evaporated filtrate gave 1.973 grams of an amorphous substance easily soluble in alcohol and water, from which it was deposited as a gummy mass, and proved in all its conduct to be the barium salt of  $\gamma$  oxy acid. Finally by exactly precipitating with sulphuric acid in the heat, and adding potassium carbonate to the cold filtrate in a narrow tube the valerolactone was obtained as a supernatant layer.

The alkaline solution freed from lactone was acidulated with sulphuric acid and distilled with steam; from the acid distillate through neutralization with calcium carbonate 0.94 gram of calcium propylideneacetate was obtained, from which the acid itself was freed. After purifying in the manner already mentioned it melted at  $7\frac{1}{2}^{\circ}$  to  $8\frac{1}{2}^{\circ}$  C.



In the process of boiling with caustic soda, there was obtained from the  $\beta$  oxy valerianic acid:

56.6 per cent. of unaltered oxy acid.

21.26 per cent. of ethylidenepropionic acid.

14.64 per cent. of propylideneacetic,

with a loss of 6.5 per cent.

*Distillation of the  $\beta$  Oxyvalerianic Acid.*—A portion of the thick, almost colorless, acid was so distilled from a small distillation flask that it passed over slowly and in drops. As the boiling began, the thermometer with its bulb in the liquid indicated  $190^{\circ}\text{C}.$ ; it was now raised until its bulb was just beneath the exit tube; it sank to  $180^{\circ}\text{C}.$ , but rapidly rose to  $190^{\circ}\text{C}.$ , where it remained constant for a short time, gradually rising to  $195^{\circ}\text{C}.$ , and then to  $200^{\circ}\text{C}.$ , where the principal portion went over, and finally to  $203^{\circ}\text{C}.$ ; the last drops of the distillate were colored yellow, and a small tarry residue only remained in the flask. The distillate, which had the same empyreumatic odor as that from methylparaconic acid, was mixed with five times its volume of water and sufficient sodium carbonate to render it distinctly alkaline after a vigorous shaking; nothing could be extracted by means of the ether, consequently, the distillate contained no lactone and a conversion of  $\beta$  oxyvalerianic acid into  $\gamma$  oxy acid respectively  $\gamma$  lactone had not taken place. The salt solution, free from ether, was now acidulated and distilled with steam, in order to separate the unsaturated acids from the oxy acid. The milky distillate was neutralized with barium carbonate and thereby the mixed barium salts of the volatile acids obtained; as, however, these can not be satisfactorily separated with alcohol, the above-described process used to effect their separation when produced by boiling the oxy acid with caustic soda was employed and the  $\beta$   $\gamma$  acid separated as lactone from the  $\alpha$   $\beta$  acid; the latter was characterized by means of its melting-point.

From the residue of the distillation with steam a small amount of the  $\beta$  oxy acid could be extracted.

The principal product in the distillation of the  $\beta$  oxyvalerianic acid was propylideneacetic acid; only a small quantity of ethylidenepropionic was found, and a like small portion of oxy acid went over unaltered.

The three isomers allylacetic, ethylidenepropionic, and pro-

pylideneacetic acids, can, as the accompanying table shows, be easily characterized and distinguished.

But recently Fittig and Mackenzie<sup>1</sup> have for the sake of simplicity, applied the terms  $\gamma \delta$ ,  $\beta \gamma$ , and  $\alpha \beta$  pentinic acids to the allylacetic, ethylidenepropionic, and propylideneacetic acids, respectively.

	Allylactic acid.	Ethylidenepropionic acid.	Propyldienacetic acid.
Free acid.	Fluid, boiling-point 186°-187° C., characteristic odor resembling that of valerianic acid.	Fluid, boiling-point 193°-194° C.	Solid melts at 74-8½° C.
Calcium salt.	Crystallize out of a hot saturated aqueous solution with one molecule of water in flat pointed prisms, which are insoluble in alcohol.	Crystallizes out of the aqueous solution in the cold, with four molecules of water of crystallization. Soluble in hot absolute alcohol.	
Barium salt.	Crystallize out of a hot saturated aqueous solution with one molecule of water in flat pointed prisms. Insoluble in alcohol.	Crystallizes in the cold out of the aqueous solution with two and four molecules of water. Soluble in hot absolute alcohol.	
Monobromide.	Both acids produce the same γ bromvalerianic acid with hydrobromic acid. Fluid and not solid at -16° C.		Gives with hydrobromic acid β bromvalerianic acid. This crystallizes out of petroleum ether in monoclinic prisms with the following forms: $\infty P_{20}, \infty P_{20}P_{20}, P_{20}P_{\infty}, P_{\infty}P_{\infty}, -P_{\infty}$ , melts at 59°-60° C. Insoluble in water, becomes liquid in water of 45°-50° C.
Dibromide.	Thin four-sided monoclinic tables melting at 58°. Difficultly soluble in petroleum ether.	Monoclinic prisms developed in the direction of the C axis. Readily soluble in warm petroleum ether; less so in cold. Melting-point 65°; dissolves in water with a gyratory motion. Becomes fluid under water of 50°-55° C.	Monoclinic prisms melting at 56°, becoming liquid under water of 15° C. Very readily soluble in petroleum ether at the ordinary temperature.

WESTERN RESERVE UNIVERSITY,  
MEDICAL DEPARTMENT,  
CLEVELAND, OHIO.

<sup>1</sup> Dissertation, Strassburg, 1894.

## THE PHOSPHOMOLYBDIC ACID TEST AS APPLIED TO LARD ANALYSIS.

BY GEORGE F. TENNILLE.

Received November 5, 1894.

THE phosphomolybdic acid test has been of late so strongly recommended for use in the detection of cottonseed-oil in lard that it seemed to the writer that the record of the results of a rather thorough trial of this reagent would be of interest to chemists.

The test was originally proposed by P. Welmans in the *Pharm. Zeit.*, 1891, 36, 798. One gram of the oil or fat was dissolved in five cc. of chloroform, two cc. of phosphomolybdic acid solution were added, and the mixture shaken. On standing, the liquid separated into two layers, the lower of which was colorless and the upper of which had become green, if any vegetable oil were present. The addition of an alkali changed the green to a blue color. Lard, tallow, goose fat, and butter fat were said not to show any green coloration, and the only animal oil which gave the test was cod-liver oil.

It was supposed that at last the reagent had been discovered which would serve to detect any addition of cottonseed or other vegetable oils to lard, no such one test having previously been satisfactory. Very shortly this reaction was recommended for such a use by a number of chemists. Among others, Engler and Rupp, Wimmer, Mansfeld, and Goske approved of its efficacy. H. Schweitzer and E. Lungwitz (*J. Soc. Chem. Ind.*, June, 1894, 614) state that they have found the reagent of great use.

Wallenstein, the first to criticise the test, (*J. Soc. Chem. Ind.*, 1893, 55) states that tallow gives a green coloration when tested with the phosphomolybdic solution. To satisfy myself in regard to this point raised by Wallenstein I have tested a large number of samples of tallow, and other qualities of beef fat—such as might be used in adulterating lard or in the manufacture of compound lard—and have in no case obtained a green color.

J. Lewkowitsch (*J. Soc. Chem. Ind.*, June, 1894, 617) has made an extended series of experiments with different fats and

oils in regard to the colors given with phosphomolybdic acid. He writes in part as follows: "Of all the samples only lard had remained colorless and there seemed to be ground for the opinion that cottonseed-oil or any other seed-oil employed for adulteration might easily be detected by phosphomolybdic acid. I prepared, therefore, a number of mixtures of pure, freshly rendered lard, yielding no coloration with Welman's test and of cottonseed-oil giving a distinct blue reaction." In testing these mixtures, he found that up to those containing thirty-five per cent. of cottonseed-oil the color of the upper layer was yellow, and at thirty-five per cent., on making this test alkaline, he only obtained a faint blue coloration. He continues: "This table clearly demonstrates the necessity of using Welman's test with great caution. In practical analysis an adulteration of ten per cent. cottonseed-oil would escape detection if freshly rendered lard had been used. Indeed, pure lard mixed with fifteen per cent. cottonseed-oil gave reactions just like sample number sixty-three in the preceding table." (Sample number sixty-three was a lard slightly rancid, six years old and gave a test remaining yellow when acid, and only faintly blue when alkaline.) "Welman's reaction can therefore be admitted only as a preliminary test, the indications of which may, in some cases, give valuable hints as to the direction in which the examination of a given sample has to be carried out and may serve as a useful corroboration of results obtained by other methods."

Of course it is understood that the original color of the phosphomolybdic acid solution is a decided yellow. The green color produced by a certain sample is not of as deep a shade as the corresponding blue color when the acid has been neutralized by ammonia. Hence a light green tinge, which would be difficult to observe on account of the initial yellow color of the reagent, would be most readily seen when changed to a blue by the alkali.

Of all the samples of cottonseed-oil, which I have tested, each one gave a green color, though I find that the color varies much in depth with different oils. It seems to be a general rule that the more refined the oil the less heavy the coloration. Thus : crude oil will color intensely green, a yellow oil perhaps less so

and a white oil still less. The age of the oil and the method of refining also in a great measure modify the color. In his tests on percentages, J. Lewkowitsch states that he used in making the mixtures a cottonseed-oil which gave a distinct blue reaction. The oil probably did not, therefore, show a deep green coloration and the test on the oil had to be made alkaline to produce a color which was decided. He must have used, I should judge, either an unusual oil or a weak solution of the reagent. For such oils as would commonly be employed for adulterations or compounding I think that ten to fifteen per cent. in a mixture would show a decided green coloration.

Samelson (*Ztschr. anal. Chem.*, 1894, 189) comes to the conclusion that the phosphomolybdic acid test is of no value and that the iodine-absorption figure is the only reliable test for the detection of cottonseed-oil in lard. He states that six samples of American lard are undoubtedly impure because they have Hübl figures of from 64.7 to 67.2, which are higher than any figures hitherto recorded by scientific investigators for pure hog fat. On this assumption hangs the result of his investigation of Welman's test.

I have often tested lards of undoubted purity for their iodine-absorption figures and obtained results as high as from 62.7 to 66.4. On the other hand, as will be seen later, the Hübl figures for pure lard can run as low as 47.7. It must be remembered that lards are sold in large amounts in the American market which do not represent the whole fat of the hog, but simply a portion. It is a well-known fact that fats from different parts of the hog vary greatly in their iodine figures, hence, lards made from different portions of the fat would also vary. Wiley (U. S. Dept. Ag. Bul., 13, Lard and Lard Adulterations, 1889), states in order to show the great difference in the absorption power for iodine of the different fats of the hog, as follows, "For instance, a sample of intestine lard absorbed 57.34 per cent. of iodine; the leaf lard from the same animal absorbed 52.53 per cent.; the foot lard 77.28 per cent.; the head lard 85.03 per cent. In the prime steam lards mentioned the percentage of iodine absorbed was from 60.34 to 66.47 per cent., and the mean 62.86 per cent." The iodine test alone would certainly not be of much service for

the detection of vegetable oils in lard, when the iodine figure of the lard itself may vary as I have found, from 44.70 to 66.40. As may be calculated, thirty per cent. or more of cottonseed-oil could be added to a lard with an iodine figure of 44.7 without the iodine figure of the mixture reaching beyond the figures of pure lard. Hence it will be seen, I think, that the condemnation of a lard as adulterated with cottonseed-oil on the ground of a high iodine figure would be hasty and might easily be erroneous.

In the literature, then, of this test up to the present time, the preponderance of the writing is in its favor, and only two legitimate limitations are placed upon its accuracy, one, that tallow might give the same results as cottonseed-oil, and the other, that a certain comparatively small percentage of cottonseed-oil might escape detection. At first blush, one would think, therefore, that the test would be of value in preliminary examinations of samples suspected of sophistication; namely, that a negative test would show the lard contained not more than ten per cent. of cottonseed-oil, and, as the addition of less than ten per cent. would hardly pay the renderer, was, therefore, probably free from vegetable oils, and that a positive test would almost conclusively point to the presence of a vegetable adulterant.

After the careful examination of a great number of lards I have come to the conclusion that a positive test does not prove the presence of such an adulteration.

In my investigation the test has been carried out as follows:

About one gram of the melted fat is placed in a test-tube and dissolved in five cc. of pure chloroform, two cc. of a ten per cent. solution of phosphomolybdic acid are then added and the test-tube vigorously shaken. After standing, and the mixture having separated into two layers, the color of the upper liquid is observed by comparison with a test run in exactly the same manner on a sample of pure laboratory rendered lard. I do not consider a test as decisive unless a very apparent green tinge appears, relying more upon the green coloration than upon the slight blue shades produced after making doubtful greenish-colored tests alkaline with ammonia.

The lards upon which most of my tests were made were of

those grades known in New York City as No. 1 lard, Prime City lard, and Prime Western lard. A brief account of the manner in which these lards are rendered and their difference in fat composition may be of help to the better understanding of their often dissimilar chemical properties. These three grades of lard make up the bulk of the lard sold to the refiners in the vicinity of New York City.

No. 1 lard generally sells at a trifle lower figure than Prime City lard, say as a limit, half a cent per pound, though often it commands the same price. It is a harder fat than City or Western and is all steam-rendered. In color it often has a distinct green tinge and will generally carry a higher steam flavor. It is rendered by the slaughterers and is made up of gut fat with once in a while a little trimmings. No leaf lard is in it as the leaf is sold with the carcass to the butchers. After slaughtering, the fat is stripped from the still warm intestines and carefully washed and goes together with a certain proportion of trimmings to the rendering kettle, where it is subjected to steam under pressure. When the process is complete the water, etc., is drained off and the lard placed in tierces for sale. This lard is made in and about New York City, the hogs being brought from the West and slaughtered here.

Prime City lard is made by the butchers and may be either rendered in open kettles with free fire or steam-rendered in the same manner as No. 1 lard. This lard sells as a usual thing one-half cent per pound below Prime Western lard. The kettle-rendered is darker in color than the steam lard and has a characteristic taste and smell.

City lard is made of the trimmings, head fat, foot fat, back-bone fat (perhaps some back fat), and any leaf which can not be sold over the counter, which fats accumulate in large amounts in the butcher shops. There is seldom any leaf lard in it as the leaf can be sold more profitably at retail for domestic rendering. The lard is usually a trifle softer than Western lard and not as good in color or flavor though better in these respects often than the No. 1 lard.

Prime Western lard is steam-rendered, of good color, high steam flavor, and a harder fat than City, but less so than No. 1.

It is rendered by the large slaughtering houses of the West in immense quantities and consists of gut fat and sometimes a little trimming.

Head fat often goes into this lard and the leaf at times may be a constituent. But only when the leaf can not be sold in the form of "neutral" lard for butterine does leaf lard find itself in the Western lard. Some back-bone fat at times may be present. The lard is shipped to the East in tierces and tank cars.

The first sample of No. 1 lard tested gave a decided green color. After further analysis the absence of any vegetable adulteration was pretty conclusively proven, and thinking that this might be a sporadic case only, samples of this grade of lard were obtained from all the firms who were rendering it in the vicinity of New York. On testing, each sample gave an undoubted green coloration, some, however, being more decided than others. After further examination of the lards it was decided that they

Hübl figure.	Titre ° C.	Rise of temperature with sulphuric acid, ° C.	Bech's silver nitrate test.	Millau's silver nitrate test.	Welman's phosphomolybdic acid test.	Microscope.	Free fatty acid. Per cent.	Specific gravity, 98° C. 15° C.
1. 54.5	41.4	30.5°	Negative.	Slight discoloration.	Decided green. Blue if alkaline.	Lard only.	...	.....
2. 55.6	41.4	31.8°	"	"	"	"	...	.....
3. 58.6	40.2	34.8°	"	"	"	"	...	.....
4. 53.7	41.4	30.0°	"	"	"	"	0.73	0.8595
5. 55.4	41.4	31.5°	slight discoloration.	"	"	"	...	.....
6. 56.1	41.4	31.7°	negative.	"	"	"	...	.....
7. 47.7	42.4	25.5°	slight discoloration.	"	"	"	...	.....
8. 51.7	41.8	31.5°	negative.	"	"	slight indication of beef.	...	.....
9. 52.0	41.9	23.5°	slight discoloration.	"	"	"	...	.....
10. 48.9	...	...	.....	.....	"	.....	...	.....

were pure hog fat. To corroborate the results a sample of the stock from which the lard is rendered was procured and after cleansing, was rendered in the laboratory. The resulting lard gave a decided green coloration with phosphomolybdic acid. The tests made upon nine samples of No. 1 lard and one sample of lard rendered in the laboratory from No. 1 lard stock may be seen in the table. Lards 1 to 9, inclusive, are those obtained



from the renderers. Lard 10 is that rendered in the laboratory.

The iodine-absorption figure was obtained in the usual manner, great care being taken in the manipulation, duplicates being run, blanks carried through with each test, and the flasks in which the determinations were made being furnished with ground-glass stoppers and gutters to hold a solution of potassium iodide seal, to prevent as far as possible any loss of iodine in vapor.

The "titre" is the crystallization temperature of the separated, washed, dried, and filtered fatty acids. The highest point which the mercury reaches, after the rise of temperature due to the liberation of the latent heat has begun, is the temperature recorded.

The rise of temperature with sulphuric acid is of no absolute value as each chemist has his own method of manipulation. The results of the test are simply given for comparison with each other in connection with the corresponding Hübl and "Titre" figures.

The Bechi test was carried out upon the glycerides using an alcoholic solution of silver nitrate. The words "slight discoloration" do not indicate the presence of cottonseed-oil which, in appreciable amounts, produces heavy blackening and often a silver mirror.

The Milliau modification of the Bechi silver nitrate test was carried out upon the fatty acids and the discoloration produced in each case was of a very slight character.

Welman's phosphomolybdic acid test on each sample showed a decided green color and on saturation of the mixture with ammonia the test turned a decided blue. By the words "decided green," in the table is meant, not a greenish yellow tinge, but a green color that was unmistakable to the eye. On the other hand, the tests were not of that deep emerald shade, such as a large percentage of cottonseed-oil would exhibit.

The microscopical examination was carried out upon crystals formed from saturated solutions of the fats in ether and showed in but one case any suspicion of the presence of beef fat, and here, sample 8, the result was doubtful.

The free fatty acid percentage was obtained in the usual way by titration and the use of phenolphthalein as indicator. The result was calculated to oleic acid.

The specific gravity was taken with a Westphal balance, the fat at a temperature of 98° C. being compared with an equal volume of water at 15° C. No correction was made for the expansion of the glass of the bob.

These lards were all hard fats with generally a high steam flavor, but with an inferior color.

It will be seen that there is quite a variation in the Hübl figures of the lards in the table; *viz.*, from 47.7 to 58.6. This is explained on glancing through the next column, when one notices that the titre decreases with approximately the same regularity with which the Hübl increases. The titre is a good guide to the hardness of the fat, that is, to the proportion of liquid to solid glycerides. As the amount of oleic glyceride increases in proportion to the amounts of stearic and palmitic glycerides, the fat becomes softer, the titre test is lower, and consequently, owing to the greater preponderance of unsaturated glyceride, the iodine-absorption figure becomes higher. The lards then owe their difference in Hübl figures to the difference in their fat composition. In the different rendering establishments, the proportion of fats used from different parts of the hog evidently varied. I consider that all the samples consisted of pure hog fat without any cottonseed or other vegetable adulteration. What constituent of this class of lards it is that has the reducing action upon the phosphomolybdic acid, I do not pretend to say. Whether it is a normal product of that portion of the fat of the hog, or simply an impurity introduced or not eliminated in the rendering process, or a peculiarity imparted to the fat at certain seasons of the year, or due to feeding, I am undecided.

Nearly all of the many samples of City lard, both steam and kettle-rendered, tested gave a negative result. In one or two cases, slight green tinges were observed. Of the fifty-seven undoubtedly pure samples tested, each representing on an average 100 tierces of lard, fifty gave no green color and seven gave a slight green tinge.

Western steam lard often gives a slight green test. Of the twenty-nine undoubtedly pure samples tested, each representing on an average 100 tierces, nineteen gave no green and ten a

slight green color. The tests were not as decided as those on the No. 1 lard but still distinctly visible. These results are probably due to the presence of the large percentage of No. 1 lard which the Western lard contains.

I might say further that lard rendered from the leaf alone, which does not, as far as I know, find its way to the lard market in this country, does not give a green color with the reagent. This fact may have been the cause of the many favorable endorsements which appeared after the first publication of the reaction. In order for the chemist to make a fair trial of the reagent, what, apparently, would appear fairer than to obtain a leaf and render it in the laboratory and make tests upon this lard?

In conclusion, I would say, that for the detection of less than ten to fifteen per cent. of cottonseed-oil the test is unreliable, as, in such an instance, no reaction may be produced. When a slight green is the result of a test, the presence of cottonseed-oil is not proven. When a heavy green color, deep emerald in shade, is obtained, the addition of a vegetable oil in considerable amounts is fairly certain. But it is easy to detect such large additions by other methods, and the phosphomolybdic test may be considered to be of slight analytical value and certainly does not fill that long-felt want of a simple test which will reliably indicate small percentages of cottonseed or other vegetable oils in lards.

LABORATORY OF THE CENTRAL LARD COMPANY,  
October 29, 1894.

## SOME NEW SOLVENTS FOR PERCHROMIC ACID.<sup>1</sup>

BY WILLIAM M. GROSVENOR, JR.

Received November 8, 1894.

ON the addition of hydrogen peroxide to an aqueous solution of potassium dichromate acidified with sulphuric acid, a blue color is produced, which is supposed to be caused by the formation of perchromic acid. Ether dissolves the blue substance, forming an intensely colored, deep blue solution. On standing, the perchromic acid in this solution decomposes with the formation of chromic acid or salts of chromium.

Recently, Griggi (*J. Chem. Soc.*, 64, 2,223) has stated that

<sup>1</sup>Read before the New York Section, December 8, 1893.

perchromic acid is also soluble in amyl alcohol, and that this solution is more stable than the ethereal solution, the color lasting for six hours. With a view to studying the behavior of perchromic acid toward certain substances, various organic liquids were tried as solvents for perchromic acid. A two per cent. solution of potassium dichromate was slightly acidified with sulphuric acid and then shaken with the solvent and hydrogen peroxide, after which it was allowed to stand. The following substances failed to dissolve the perchromic acid:

Carbon disulphide, benzene, ligroin, spirits of turpentine, castor oil, oil of wintergreen, oil of bergamot, kerosene, paraffin oils, chloroform, carbon tetrachloride, toluene, nitrobenzene, and aniline.

The following substances were found to be solvents for perchromic acid:

Ethyl acetic ester, valerianic ether, amyl valerianic ester, amyl chloride, amyl butyric ester, amyl formic ester, and amyl acetic ester.

In order to determine which of the solutions of perchromic acid lasted the longest, the following experiments were made. Equal amounts of a dilute solution of chromic acid were shaken in the presence of the solvents with equal amounts of hydrogen peroxide, in small oil-sample bottles, and allowed to stand on a window frame exposed to a strong light. The temperature varied from 10°-20° C. The results were as follows:

Amyl alcohol retained its color one hour and ten minutes, then turned brown.

Amyl chloride retained its color one hour and fifty-five minutes, then turned colorless.

Amyl butyric ester retained its color one hour and fifty-five minutes, then turned brown.

Amyl valerianic ester retained its color two hours and ten minutes, then turned green.

Valerianic ether retained its color two hours and thirty-five minutes, then turned colorless.

Amyl formic ester retained its color sixteen hours and fifty-five minutes, then turned white.

Amyl acetic ester retained its color seventeen hours and fifty-five minutes, then turned colorless.

Ethyl ether retained its color eighteen hours and twenty-five minutes, then turned colorless.

Ethyl acetic ester retained its color twenty-three hours, then turned colorless.

These results do not agree with the observations of Griggi, that the amyl alcohol solution of perchromic acid is more stable than the solution in ether. The most stable solution is that in ethyl acetic ester. The time of duration given by Griggi, six hours, was evidently found under different circumstances. If the layer of the solvent is allowed to remain upon the aqueous layer the decomposition of the perchromic acid is greatly accelerated. The above experiments were made in this manner. Those of Griggi may, perhaps, have been made under other conditions in this respect.

CHEMICAL LABORATORY OF THE BROOKLYN  
POLYTECHNIC INSTITUTE.

### SOME FACTS OBSERVED IN THE DETERMINATION OF PHOSPHORIC ACID BY THE MOLYBDIC ACID PROCESS.

BY RUDOLF DE ROODE.  
Received November 26, 1894.

THE length of time necessary for the complete precipitation of phosphoric acid seems to be much less than is generally supposed. Portions of the same solution were treated with molybdic solution and allowed to stand at 65° C. for five, ten, fifteen, twenty, thirty, forty, fifty, and sixty minutes, respectively, and two portions stood in a warm place over night. The phosphoric acid determined as usual as magnesium pyrophosphate, showed that the precipitation was complete after standing only five minutes. The weights of magnesium pyrophosphate were as follows:

5 minutes.....	0.0676 gram	} Average 0.0673
10 " .....	0.0672 "	
15 " .....	0.0674 "	
20 " .....	0.0672 "	
30 " .....	0.0669 "	
40 " .....	0.0670 "	
50 " .....	0.0673 "	
60 " .....	0.0675 "	
12 hours.....	0.0671 "	
24 " .....	0.0676 "	

By making a determination of phosphoric acid, using twenty-

five cc. of a very dilute sodium phosphate solution and the same quantities of reagents as are used in a regular determination, and then adding twenty-five cc. of this same dilute sodium phosphate solution to a regular determination and using the first determination as a blank which is subtracted from the last, we get a lower result, which would seem to indicate that a regular determination, without the addition of the phosphate solution and subtraction of the blank, gives too high a result.

A dilute sodium phosphate solution (twenty-five cc.) gave, with the same quantities of reagents as ordinarily used,

1.....	0.0158	gram of magnesium pyrophosphate.
2.....	0.0161	" " "
3.....	0.0156	" " "
4.....	0.0163	" " "
5.....	0.0160	" " "
<hr/>		
Average....	0.0160	" " "

Twenty-five cc. of an acid phosphate solution, together with twenty-five cc. of the above sodium phosphate solution and the same quantities of reagents gave

	0.0821	gram of magnesium pyrophosphate.
Blank.....	0.0160	" " "
<hr/>		
Difference....	0.0661	" " "

The average of the ten results obtained where no blank was subtracted was 0.0673 gram magnesium pyrophosphate, making a difference of 0.0012 gram.

Three of the weighed precipitates of magnesium pyrophosphate, in the series of ten, were redissolved in nitric acid, and reprecipitated with molybdic solution and magnesia mixture, ignited in the same crucibles and weighed. At first the magnesium pyrophosphate weighed :

1 .....	0.0672
2 .....	0.0670
3 .....	0.0671

After solution and reprecipitation :

1 .....	0.0660
2 .....	0.0660
3 .....	0.0659

Again dissolved and reprecipitated as before :

1 .....	0.0659
2 .....	0.0658
3 .....	0.0657

There seems to be no further loss on reprecipitation, and the results, after the second and third precipitation, agree closely with the results obtained by using and subtracting a blank. These results also would indicate that somewhat too high results are obtained by the regular method for phosphoric acid determination.

Another fact along this same line was also observed ; *viz.*, that if different quantities of the same phosphate solution are precipitated, the larger quantity gives the lower and more correct result. Thus, twenty-five and fifty cc. of a phosphate solution, precipitated as usual, gave quantities of magnesium pyrophosphate which, when expressed in percentage of  $P_2O_5$ , were :

Twenty-five cc. gave 26.05 per cent. and 26.10 per cent.

Fifty cc. gave 25.96 per cent. and 25.97 per cent.

And another solution in like manner :

Twenty-five cc. gave 36.38 per cent.

Fifty cc. gave 36.18 per cent.

The most plausible explanation of this also seems to be that there is some source of error tending to give too high a result, which is multiplied more the smaller the quantity which is taken, and it would seem desirable, for the sake of accuracy, to employ as large a portion as is convenient.

The foregoing experiments seem to warrant the following conclusions :

1. That our present method for determining phosphoric acid seems to give results which are somewhat too high.
2. That the results obtained by using a large quantity of substance, and obtaining large precipitates, are lower and somewhat more accurate than those obtained where smaller quantities are employed.
3. That somewhat lower and more accurate results are obtained by using a blank made by employing a dilute solution of a phosphate, which is added to each determination. This blank, previously determined, being subtracted from the final result.
4. That accurate results, agreeing with those obtained by the

use of the blank, are obtained by redissolving the magnesium pyrophosphate and reprecipitating.

5. That five minutes digestion at 65° C. seems to be sufficient for the complete precipitation of phosphoric acid by molybdic solution.

AGRICULTURAL EXPERIMENT STATION,  
MORGANTOWN, WEST VIRGINIA,  
November 12, 1894.

## THE ADDITION OF CALCIUM CHLORIDE TO THE SOLUTION OF A FERTILIZER IN THE DETERMINATION OF POTASH.

BY RUDOLF DE ROODE.  
Received November 26, 1894.

MR. H. A. HUSTON has proposed the addition of a solution of calcium chloride to the solution of a fertilizer in the determination of potash, in order to furnish sufficient calcium to form tricalcium phosphate with all the phosphoric acid present, and thereby permit of the use of platinum dishes in the Lindo-Gladding method. In testing this proposition I find that when sufficient calcium chloride was added to combine with all the phosphoric acid present and then ammonia added in excess and a portion of the solution filtered off, no test for phosphoric acid could be obtained. But, that if in addition to the calcium chloride and ammonia, some ammonium oxalate or carbonate was added, a filtered portion of the solution *did* give a test for phosphoric acid. This is accounted for by the fact that the calcium phosphate, which was precipitated by the ammonia, is changed by the ammonium oxalate or carbonate into calcium oxalate or carbonate and ammonium phosphate, so that the very object for which the calcium chloride was added is defeated by the addition of the ammonium oxalate or carbonate. In order to make the use of calcium chloride effective it is necessary to filter off from the precipitate formed by the calcium chloride and ammonia and to then add the ammonium oxalate or carbonate to the filtrate. This necessitates two separate filtrations, and it is doubtful if we have in Mr. Huston's suggestion anything better than, or even so good as in the present alternate method.

AGRICULTURAL EXPERIMENT STATION,  
MORGANTOWN, WEST VIRGINIA,  
November 12, 1894.



## ON THE PREPARATION OF AMMONIUM CITRATE SOLUTION.

BY RUDOLF DE ROODE.  
Received November 26, 1894.

**M**ANY times in preparing a solution of ammonium citrate, I have observed a fact which seems to indicate that the preparation of a strictly neutral solution is an extremely simple matter. If some citric acid is treated with ten per cent. ammonia until dissolved, the solution becomes quite hot, and if it is now diluted to nearly the proper specific gravity, made decidedly alkaline with ammonia, and allowed to stand over night in an open dish, it will be found in the morning to be strictly neutral.

Being warm and in an open dish the excess of ammonia escapes completely, leaving it neutral. For the last four or five times which I have had occasion to prepare an ammonium citrate solution, I have observed this fact and each time have found it unnecessary to alter the neutrality in the least degree. I find it very convenient. I also find it advantageous to add a small quantity of salicylic acid to the solution (about one gr. for five liters of solution is sufficient). This is added before neutralization, so that the salicylic acid is also neutralized by the ammonia. The salicylic acid prevents the growth of fungus in the solution and it remains unchanged a long time. Some solution six months old when used in fertilizer work, gave results practically identical with those obtained by the use of a freshly prepared solution.

AGRICULTURAL EXPERIMENT STATION,  
MORGANTOWN, WEST VIRGINIA,  
November 12, 1894.

---

## THE DETERMINATION OF POTASH IN MANURES.

BY W. E. GARRIGUES.  
Received November 15, 1894.

**T**HE following method for the determination of potash in fertilizers, has been in use in the writer's laboratory for some months, and in view of its ease, quickness, and comparative accuracy is believed to be a decided improvement on that of Lindo-Gladding.

It depends upon: 1. The ignition of the material with sul-

phuric acid, thereby converting all potash present, to sulphate, if not already in that form, and at the same time expelling any ammonia and organic matter. 2. Precipitation of the sulphuric acid with barium chloride. 3. Precipitation of the excess of barium, together with other earthy bases, by sodium carbonate. 4. Evaporation of the filtrate with platinic chloride as usual.

The process entails but one filtration and evaporation and with due precaution the final precipitate of potassium platinochloride is obtained practically chemically pure.

The analysis: Ten grams of the sample are weighed into a platinum dish and worked into a paste with concentrated sulphuric acid. The rod is wiped with a small piece of filter paper, which is added to the sample, and the whole ignited, raising the heat gradually and finishing with a blast until the residue is white, or red if much iron be present.

The contents of the dish are now scraped out into a porcelain mortar and ground to a fine powder, a little hot water is added, washing out the dish at the same time, and the mass triturated for a few minutes. It is next washed into a 500 cc. flask and boiled with 250 cc. of water for half an hour, when a ten per cent. solution of barium chloride is run in five cc. at a time and boiling after each addition, until no further precipitation is visible.

Add a single drop of phenolphthalein solution and sodium carbonate, drop by drop, until a faint permanent rose color is obtained. Boil for a minute, set aside to cool, and make up to the mark. Filter through a dry paper and measure out fifty cc. of the filtrate = one gram of sample. Add hydrochloric acid to slight acid reaction, as shown by the disappearance of the rose color, and evaporate on a water-bath with platinic chloride. Wash the precipitate with alcohol, sp. gr. 0.848 (= eighty per cent. by weight), dry at 100° C., and weigh. For potash salts, the ignition with sulphuric acid is omitted.

Remarks: 1. The sulphuric acid must be added cautiously as fertilizers containing chlorides and nitrates react somewhat violently, endangering loss of the assay. 2. It is important that the ignited mass be very finely pulverized, otherwise the calcium sulphate, most of which remains insoluble, will mechanically enclose the potassium sulphate and prevent its complete

solution. 3. An excess of sodium carbonate is not permissible as double decomposition with the precipitated barium sulphate may take place, leaving sodium sulphate in solution and rendering erroneously high results. 4. It is recommended to turn the flame under the bath below boiling temperature when the solution has evaporated to small bulk. In case it then goes to hard dryness, no harm is done, while, if the bath be boiling, it is necessary to keep a close watch lest this occur. 5. For the filtration and weighing, a Gooch crucible, fitted with a single disk of filter paper, leaves nothing to be desired.

This method was first adopted as a safe one, on its favorable showing when checked against the Lindo-Gladding, and has, since proven in the writer's hands very much more concordant than the latter. Since the publication of Mr. Norman Robinson's criticism of several well-known methods of potash determination (This JOURNAL, 16, 364), the writer has made a more careful investigation of the value of this process, comparing it with two others and incidentally confirming some of Mr. Robinson's work.

It was thought most satisfactory to operate on samples of known composition, and with this end in view several, representing the usual variety met with in commerce, were prepared. In each case the potash "occluded" by the various precipitates was determined after washing until no reaction with silver nitrate was visible. To facilitate comparison all the figures are given in per cent. potassium oxide.

Nature of Sample.	Calculated content potassium oxide.	Found by Lindo-Gladding.	Recovered from precipitates.	Found by Stassfurt.	Recovered from precipitates.	Found by Garrigue's.	Recovered from precipitates.
Complete Fertilizer; containing $K_2SO_4$ .	5.40	5.16	0.20			5.17	0.09
		5.28	0.11			5.19	0.12
						5.25	0.09
						5.28	0.17
Complete Fertilizer containing KCl.	6.31	6.12	0.15			6.22	0.08
		6.09	0.14			6.14	0.12
Mixed salts KCl+CaCl <sub>2</sub> +MgSO <sub>4</sub> .	63.17	63.19	0.12	62.85	0.19	62.75	0.18
		62.74	0.15	62.80	0.17	62.95	0.15

The figures under the headings of the three methods do not include the per cent. recovered from precipitates. In the Stassfurt method the quantity of barium chloride necessary was calculated and exactly added, so that no doubt need exist as to the potassium platinochloride obtained having been contaminated with sulphates on an excess of barium chloride. In one case the total return by the Lindo-Gladding method was apparently more than was present, due no doubt to a slight contamination with calcium sulphate. It should be remarked that no corrections were made for the volume occupied by the precipitates in the flasks. The factor used in calculating the double chloride to potassium oxide was 0.193.

The writer is frank to acknowledge that frequently the Lindo-Gladding method has given him very discordant results. This has been especially noticeable in fertilizers containing liberal amounts of potash. An aggravated case of the kind was a return in triplicate of 10.16-11.37-12.75. The writer's method gave 12.73-12.76 and an experiment station working on the same sample found 13.10. Two other instances of disagreeing duplicates by the Lindo-Gladding process are 4.76-5.07, and 6.10-6.54.

It is difficult to give any satisfactory reason for these discrepancies, as they are probably due to a multiplicity of causes. The writer has always felt the re-solution of the ignited potassium sulphate in water to be an unsatisfactory step and this alone sufficed to make the adoption of a new method desirable to him, the official alternate method being too tedious for ordinary use.

It is suggested that the material differences among chemists working by the Lindo-Gladding method, may be, in part, due to the varying strength of the alcohol-wash. The official directions, though they mention eighty per cent., do not lay sufficient stress on this point. If ninety, or even eighty-seven, be used in the second washing, ammonium chloride is precipitated with consequently higher returns.

In conclusion, while it is plain the method here proposed does not, in common with those now in use, return quite all the potash, it is seemingly less accurate than none and certainly less discordant than the Lindo-Gladding, besides being more satis-

factory to work, and quicker. It obviates the no small difficulty of precipitating all the sulphuric acid without adding an excess of barium chloride in the Stassfurt, and avoids the tedious evaporations and filtrations entailed by the alternate. Against all these advantages there has appeared so far only one disadvantage: the necessity of using a greater quantity of platinic chloride.

### THE RAPID AND ACCURATE ANALYSIS OF BONE-BLACK.<sup>1</sup>

BY W. D. HORNE, PH.D.

SEVERAL years' experience in the analysis of bone-black have led me to the adoption of the following method for attaining accurate results with comparative rapidity.

In new char, bought from the dealer, the determination of moisture is of importance, being frequently limited by contract to three per cent.

In char, in constant use in sugar refineries, the moisture in the revived sample is of no importance under usual conditions.

The moisture is determined by heating two grams of the unground char for two hours in a hot air-bath at 140° C. It can be weighed between watch-glasses held by a clip to prevent absorption of moisture.

A convenient way of estimating calcium carbonate is with Lunge's nitrometer, using mercury. Two grams of the finely pulverized sample are introduced into a two-ounce Erlenmeyer flask and moistened with three cc. of a saturated solution of mercuric chloride, the tube of ten cc. of hydrochloric acid (sp. gr. = 1.12) introduced and the flask closed with a rubber stopper, which, with a short glass tube and a rubber tube, is hung to the tube of the three-way cock. By tipping the acid out upon the char and properly manipulating the stop-cock the carbon dioxide is liberated, collected, and measured. Any hydrogen sulphide given off is absorbed by the mercuric chloride. Corrections are made for temperature and atmospheric pressure.

For the determination of carbon, iron, calcium sulphate, and insoluble ash, one portion is used. In preparing the sample

<sup>1</sup> Read before the New York Section, November 9, 1894.

for analysis the iron particles must first be removed by a magnet and the char then ground to an almost impalpable powder.

Two grams of this are moistened with water and treated in a four-ounce covered beaker, with twenty cc. hydrochloric acid, and boiled gently until solution is complete, which is within thirty minutes. The beaker is filled up with boiling water and after settling, which takes place almost immediately, decanted upon a weighed platinum Gooch crucible with asbestos plug. The carbon is washed by decantation in this way five or six times, until the filtrate is free from chlorine. The original filtrate and first decanted washing contain practically all of the iron and calcium sulphate. The following wash-waters can usually be rejected. The carbon is washed out of the beaker into the Gooch, and is then washed with eighty per cent. alcohol, ninety-five per cent. alcohol and ether, each two or three times, set in a water-jacketed air-bath, and heated at  $100^{\circ}$  C. to a constant weight, which will take about three hours. The increased weight is due to carbon and ash. The carbon is burned off over the blast. The loss of weight is then carbon, and the difference is ash.

To the acid solution containing iron and calcium sulphate a drop of methyl orange solution is added and ammonia to nearly neutral reaction. Ammonium acetate is added until the solution turns yellow and then a few drops in excess. The solution is now heated below  $70^{\circ}$  C. until complete precipitation of iron and aluminum phosphate takes place, which is usually in about twenty minutes. The precipitate, after being washed free from chlorides, is dissolved by dilute sulphuric acid into a six-ounce Erlenmeyer flask, ten cc. of a ten per cent. solution of sodium sulphite added, and boiled to reduce the iron and to expel the sulphur dioxide. To ascertain when this gas ceases to come over, the vapor is led from the flask through a glass tube fitting through the rubber stopper and inclining vertically downward at its outer end. Under this is held a test-tube of dilute potassium permanganate acidified with sulphuric acid. So long as sulphur dioxide, issues it will decolorize the permanganate solution in the tube when the gas is caused to bubble up through the upper half inch of the solution. When the sulphur dioxide

is all out a drop of the solution from the flask is tested with potassium sulphocyanide for ferric iron. When the reduction is complete the solution is cooled and titrated with permanganate. If alumina is to be determined the above-mentioned precipitate of the iron and aluminum phosphates can be treated with 150 cc. of ammonium molybdate solution, to precipitate the phosphoric acid, and filtered. In the filtrate iron and alumina are precipitated as hydroxides by ammonia, filtered off, dissolved in hydrochloric acid, reprecipitated with ammonia, collected, ignited, and weighed. The two may then be separated by any of the well-known methods.

The filtrate from the iron and alumina precipitation contains the calcium sulphate. This solution is acidified with hydrochloric acid, and barium chloride added to precipitate the sulphuric acid. The barium sulphate is treated in the usual way and calculated to calcium sulphate.

Calcium sulphide may be determined by treating five grams of char with twenty cc. of nitric acid and evaporating nearly dry, adding twenty cc. of hydrochloric acid, and evaporating again very low to expel nitric acid, taking up in hydrochloric acid, and in an aliquot portion of the filtered solution precipitating the sulphuric acid in the usual way with barium chloride. From the weight of barium sulphate found, is deducted that found as above, due to calcium sulphate. The remainder is that due to calcium sulphide.

The physical condition of the char is of great importance and should be thoroughly examined into. The grist is estimated by throwing 100 grams upon a sieve of known mesh, shaking gently, and weighing what passes through. This portion may, in turn, be passed through successively finer sieves, and weighed after each. In shaking the sieve should be tapped only very gently—otherwise particles of char will be forced through which, correctly, belong above.

To determine the density of the char it should be carefully filled into a weighed flask of 50 or 100 cc. capacity, and of very gently sloping sides. Admitted into such a flask through a funnel the char fills it completely without leaving vacant recesses at the shoulders. This is weighed, from which is cal-

culated the specific gravity of the char when loose and the pounds per cubic foot. Now the flask is tapped lightly on the table and as the char settles down more is added until no further settling takes place, and the flask is filled to the mark. This gives the weight of char when packed, from which may be calculated, as before, the specific gravity and weight per cubic foot.

As char grows old in use its porosity decreases and its specific gravity increases. It is sometimes desirable to know its porosity. To do this the weighed flask is filled with distilled water, the char introduced, little by little, displacing part of the water from the flask. At the same time the water remaining displaces from the char its contained air, which rises in minute bubbles. The flask is tapped to pack the char, and, when filled to the mark, is heated on the water-bath to expel all air. After cooling, the supernatant water is removed and the flask and contents weighed. The increased weight over that of the flask packed with char is that of the contained water, from which can be calculated the capacity of the char for any liquid of known specific gravity.

The repeated handling which bone-black receives in continued use in sugar refineries, etc., tells on it very seriously, as the friction of the grains against each other and the machinery wears it into dust. This change is slow, but in the long run is very costly, as the fine dust has to be discarded and replaced by new char.

Any method, therefore, which would enable one to judge of the relative durability of samples of char under this continued friction should be worthy of consideration. I have attempted to contrive such a test, and after a good many experiments have found one which promises well. Twenty-five grams of the char to be tested, between sixteen and twenty-four grist, approximately, are thrown on a sieve with circular holes, one-fiftieth of an inch in diameter, the sieve shaken back and forth ten times, tapped three times, and the shaking and tapping repeated twice. This drives the dust through, and it is weighed. Dust and char are then both put into a cylinder of tinned iron, four inches in diameter, and two inches deep; then six glazed porcelain marbles five-sixths of an inch in diameter and weighing together 74.66 grams are added. Now the can is shaken back and forth



with slightly rotary motion 200 times, the marbles removed, and the char sifted as before. The increased weight of dust is calculated to per cent. of the char used. These tests are pretty constant for different portions of the same sample of char.

The dust formed thus from a good new char was in three cases 1.72 per cent., 1.46 per cent., and 1.76 per cent. From another new char 2.68 per cent. and 2.44 per cent. Two grades made by one firm gave 2.16 per cent. and 2.16 per cent. in one case, and 2.86 per cent. and 2.87 per cent. in the other. Char which had been in use ten months and whose softer parts had already been separated by use gave 0.92 per cent. and 0.94 per cent., showing that it was then in a better wearing condition than when it first entered into use.

---

### THE ASPHALT QUESTION.

BY S. F. PECKHAM.

THERE has lately been published some very interesting reading concerning this question. To go back a few months, in October, 1892, Consul Pierce made a report that seemed to leave very little to be said in reference to Trinidad asphaltum from any standpoint. A few months later, Mr. Clifford Richardson published in the *Journal of Analytical and Applied Chemistry*, for Dec. 1892, and Jan. 1893, a paper in which he embodied the results of a most elaborate series of technical analyses of Trinidad asphalts. Within the last twelve months there has been published a voluminous report on Trinidad asphalt by Mr. Richardson, in the "Mineral Resources of the United States." In several late numbers of *Paving*, Mr. D. Torrey has shown that a method of analysis of asphalts may be based on successive solutions in alcohol; and he has also discussed in a very suggestive and intelligent manner, the general subject. In the July number of *Paving*, Messrs. Richardson and Bowen pay their respects to the report of Messrs. Leffman and Sadtler, made to the Citizens' Municipal Association and Trades League, of Philadelphia. In the August number of the same journal Messrs. Leffman and Sadtler reply to their critics. In the December number of this JOURNAL Miss Laura Linton publishes a paper, in which she gives the result of a very careful

research upon the methods heretofore employed in the technical analysis of asphalts. I am also just in receipt of a report upon "The Gas and Petroleum Yielding Formations of the Central Valley of California," by W. L. Watts, of the State Mining Bureau.

I propose, by a general review of these papers, to ascertain where a chemist, who is occasionally consulted in reference to asphalt, might reasonably take his stand.

It is now about fifty years since I first noticed, in a number of the *Penny Magazine*, an illustrated article on the "Pitch Lake of Trinidad." My interest in this wonderful phenomenon has never abated. Somewhere late in the fifties, when the Downer Kerosene Oil Co., was ransacking everywhere, but in Pennsylvania, for crude material for illuminating oil that was cheaper than Boghead Mineral, or Albertite, the late William Attwood was sent to Trinidad, where he remained two or three years. Several years after his return it was my good fortune to meet him, and I listened with eager interest to his description of the so-called lake, which he represented as a mass of asphaltum of unknown depth, floating upon a veritable lake of water. His experiments in the line of preparing illuminating oil from the asphalt were so far from a success that the late Samuel Downer once facetiously remarked, that the Trinidad pitch was, without doubt, derived from right-whales, black-fish, etc., while Pennsylvania petroleum was certainly nearly pure sperm oil. Later investigations have shown that both Mr. Attwood and Mr. Downer were considerably mistaken in their conclusions.

The report of Consul Pierce shows that the so-called pitch lake has no definite boundaries, but overflows towards the sea, over the rim of its irregularly circular basin, on one side. His report also shows that the sources from which the bitumen rises to the surface, are not confined to the strata beneath the so-called pitch lake, but are also found in the strata that underlie that portion of the island of Trinidad adjacent to the lake, to such an extent that unknown areas are covered with masses of asphalt, of unknown thickness. This asphalt, from both inside and outside the lake, was mined and sold, but that from outside the lake was finally distinguished as "land asphalt" by those who chose to

do so. Consul Pierce shows conclusively that the same cosmical forces that bring asphaltum to the surface in large quantity at the lake, bring it to the surface at many other points upon the island in smaller quantity, and, that other things being equal, the asphaltum is the same thing in both instances.

In Mr. Richardson's elaborate paper above referred to,<sup>1</sup> he gives results of analyses of a number of specimens that were taken from the lake, and compares them with corresponding results of analyses of a number of specimens taken from the land. He admits that no practical difference can be shown to exist between good commercial samples from either source; but he insists on introducing analyses of lake asphalt that are too soft for commercial purposes, and also of a lot of land specimens that, so far as serving any useful purposes are concerned, are neither more nor less than rubbish. No one familiar with deposits of surface asphalt in Southern California, would visit an asphalt bed and dignify the refuse from the numerous fires that, from immemorial periods, have swept over its surface, with the names of "iron-pitch," etc., and think an argument necessary to prove that the ashes, cinders, coke, and half-burned asphaltum, are unfit for street payement. I have seen masses of coke, from fifteen to eighteen inches thick, taken from burnt asphalt beds, and thousands of tons of melted and half-burned asphaltum, in streams miles in length, the analysis of which would afford most convincing proof that they were unsuitable for street pavement. Setting aside the soft pitch on the one hand, and the rubbish on the other, it appears to me, that any unprejudiced person must admit, that Mr. Richardson's paper proves either too little or too much; either that the methods and material he used proves nothing, as is really the case, or that the results he has obtained prove the practical identity of "lake" and "land" asphalt of good commercial quality.

In the report by Mr. Richardson in "Mineral Resources of the United States for 1893," he goes into the history of the paving industry, and gives some very interesting details, both political and commercial, the argument of which appears to be that while there are other asphalt paving materials to be had in the

<sup>1</sup> *J. Anal. Appl. Chem.*, Dec. 1892, and Jan. 1893.

world, the only material worth considering is that laid by the Barber Asphalt Paving Co., that use and practically own the "lake" deposit, which, after all, is not a lake at all, but fills "the crater of an old mud volcano." He says, "in times past it appears that the continued welling up of pitch at the center of the lake filled the crater and caused it to overflow towards the sea." Here again, he either proves that the whole of the pitch is worthless, or that the whole deposit outside and inside the crater is practically one and the same thing.

He starts into the discussion of the Technology of Trinidad asphalt pavements, with the important information that "The crude pitch is shipped from La Brea in Trinidad in both sailing vessels and steamers." Farther on, he shows by a sort of historical résumé, that a little more care has lately been taken in refining the pitch than formerly, by which the damage resulting from prolonged overheating is avoided to some extent. He then grapples with the cement problem. He says of the fluxing oil, "it should not contain large amounts of hard paraffins, for in this case, while it may be of suitable nature for making cement at ordinary temperatures, it is susceptible to changes and makes the resulting cement too brittle at low temperature and too soft in heat of hot summer sun. The more the oil is of a vaseline nature the better it is. While the oil now in use is a great advance over that of some years ago, there still seems to be room for improvement. "The character of an oil may be learned by determining—

1. Specific gravity.
2. Flash-point.
3. Percentage volatile in seven hours at 400° F.
4. Susceptibility to changes in temperature as revealed in changes in viscosity.
5. Presence of crystals of paraffin scale.

Before mixing, the asphalt is raised to a temperature of 300° F., or thereabout, and to produce rapidly a smooth mixture, the oil should be heated as hot as is convenient. The oil is then pumped or in other ways added to the still, and the mixture agitated for several hours with a current of air until it is quite homogeneous. This agitation must be done with great thor-

oughness to insure a uniform cement, and must be continued whenever the material is in a melted condition, as a certain amount of separation takes place when the melted cement stands at rest. It is, therefore, customary to agitate it constantly with an air-blast when in use as well as in its preparation."

Then he goes on to describe the ingenious toy with which Prof. Bowen, of Columbia College, amuses himself. This instrument is so delicate that, "as the needle (a cambric needle) is not at a normal temperature an allowance must be made." Comment is unnecessary.

In a paper that I read at the Congress of Chemists,<sup>1</sup> held at the Columbian Exposition, I took the position that the residuum in use for softening asphalt that is made from petroleums consisting of paraffins, and that consequently contains paraffins, is not a solvent for asphaltum, and therefore is not a suitable material for an asphaltic flux; as when an attempt is made to incorporate the two materials, the result is a mechanical mixture and not a chemical union as it should be. I based my argument on the results of laboratory experiments, and I now gladly welcome Mr. Richardson to my side, as his very emphatic statements are based upon the much stronger proof of practical experience. In the paper above referred to I further maintained that the custom of "blowing" asphalt, or mixing it by the use of a current of air injected into the molten mass while heated to a high temperature, is all wrong.

Mr. Richardson writes well, and he uses the word "scientific" in a way that sounds well; but I hazard the opinion, that if he read more and wrote less, his opinions would have more weight. The first "scientific" paper in which the effect of the prolonged heating of bitumens was discussed, was published by Boussingault in 1837. He says,<sup>2</sup> "after different experiments, the means that I have finally employed in order to free the bitumen of its volatile principles, consists in exposing it at a temperature of about 250° (C. = 480° F.?) in a Gay-Lussac oil-bath until it no longer loses weight. This method is prolonged, as it is necessary to heat during forty-five to fifty hours, even when operating

<sup>1</sup> Mineral Resources of the United States, 1893, 651.

<sup>2</sup> *Am. J. Sci.*, Jan., 1894; *Paving and Municipal Engineering*, Aug., 1894.

<sup>3</sup> *Ann. chim. phys.*, 64, 141.

on only two grams of material." In a note he adds, "By this method it is impossible to determine the two principles of the bitumen, as at that temperature a part of the petroleum is oxidized and passes to the solid state or asphaltene." Technologists in petroleum have known for years that prolonged heating will convert paraffin petroleums into a solid residuum. It has also been known for years that California petroleums can be so manipulated by heat as to convert a large percentage of them into an asphaltic residuum, that will contain varying proportions of material soluble in petroleum ether, carbon disulphide, and chloroform, leaving a residue of coke, according to the temperature to which it has been heated. The percentage of material soluble only in chloroform increases also in proportion to the time during which it has been heated. A patent has lately been issued from the U. S. Patent Office for a method or process for preparing these residues.

It seems incredible, that the scientific adviser of a great corporation, that has the reputation of seeking to control the asphalt paving business of the United States, should be ignorant of these facts. Why then this space occupied in the Mineral Resources of the United States, with descriptions of technological processes, that all of the knowledge possessed by the scientific world for the last sixty years, condemns as unscientific?

Mr. Richardson has taken great pains to show that he found a good quality of "land asphalt," that contained, if I remember his figures, two per cent. less of matter soluble in petroleum ether than a fair quality of "lake asphalt." This difference he regards as absolutely exclusive of "land asphalt" for paving purposes. He then describes how this "lake asphalt" is refined. He does not say whether refined lake and land asphalt differ by two per cent. of matter soluble in petroleum ether or not. He then shows how the refined lake asphalt is softened with a material that, according to his own showing, will not form even a mechanical mixture with the melted asphalt except by constant agitation with a current of air, and that, up to the point when the so-called cement is put into its final resting place upon the street. It is a fair question, whether lake asphalt after this wholly unscientific treatment does not contain a larger percentage of matter insol-

ble in petroleum ether than would land asphalt, when properly manipulated.

Mr. Richardson says, " Washington has had more experience with sheet asphalt pavements and more time and attention have been devoted to both the scientific and practical sides of the industry there than in any other city in the country." If Mr. Richardson has faithfully represented the state of the art in this highly favored city, in what condition must the rest of the country be found where scientific principles have not been introduced into the industry?

Mr. Richardson has been giving his attention to the scientific principles underlying this industry for a number of years. I think it may be safely said that he has had a better opportunity to become an acknowledged scientific authority upon this subject than any chemist living. After what manner has he used this opportunity? He has published a large number of so-called analyses of asphaltum. When making these analyses he either found a method already in use, which his experience proved to be satisfactory, or he invented a better one. In either case, by long continued use, he made the method his own. I am not aware that he has anywhere described his method of analysis, but the terms in which he has stated the results of his analyses, indicate his method with sufficient clearness. He states the amount of water, the percentage soluble in petroleum ether, the percentage soluble in carbon disulphide, the percentage of organic matter not bitumen, and the percentage of inorganic or mineral matter. It is a fair assumption that with Mr. Richardson's opportunities, he thoroughly investigated every step in this process of analysis, and is prepared to show that water, and not volatile oils or gases, are determined as water; that either petroleum ether of any sp. gr., *e. g.*, any light distillate of petroleum can be used in place of any other, with the same results, or that a distillate of a particular sp. gr., obtained from a particular petroleum should be used. It is further to be presumed, that he is able to show that petroleum ether is the best liquid that can be used for this purpose, and that the separation made by its use is sharp and clearly defined. It is further to be

<sup>1</sup> Mineral Resources of the United States, 1897, 653.

presumed, that when this residue from which petroleum ether has made a complete solution, is subjected to the action of carbon disulphide, that setting aside the difficulty of obtaining the reagent pure, its action is attended with no serious objections and is complete ; that is, it dissolves every trace of bitumen remaining in the residue. All of this should have been proved beyond question years ago. But Mr. Richardson has apparently allowed that two per cent. of difference between lake and land asphalt to so obscure his mental vision that he has left it to the careful and painstaking accuracy of Miss Linton to show that carbon disulphide will not dissolve completely the bitumen from asphaltum, and that boiling spirits of turpentine is an equivalent for carbon disulphide, and is a much more convenient and satisfactory reagent to use.<sup>1</sup>

There are mistakes to which every one is liable and that are properly to be excused ; there are others that are absolutely without excuse. I confess, that to my mind, there is no excuse for a man, who, occupying the position or responsibility that Mr. Richardson has occupied, publishes the results of analyses year after year, upon which, as a basis, it has been sought to influence the expenditure of millions of public money, when, in reality, he has made no proper investigation of his processes, and knows nothing respecting the accuracy or proper significance of his results. Mr. Richardson has no right to complain if his constituency hereafter repudiate all of the dicta that he has with, I had almost said, unpardonable arrogance thrust upon the public, in reference to the "Asphalt Question."

I have read the articles of Mr. Torrey with a great deal of interest.<sup>2</sup> They are suggestive. I have not found, by experience, that his method of analysis by solution in alcohol, promises any superiority over that proposed by Miss Linton. The test of a method of analysis is, other things being equal, the parallelism shown in the results when duplicate analyses are made, side by side. In one instance, with her process, I have obtained results parallel to the third place of decimals. Such close correspondence in work of this kind is not generally to be expected ;

<sup>1</sup> This JOURNAL, 16, 809.

<sup>2</sup> *Paving and Municipal Engineering*, Nov., 1893 ; April, May, and September, 1894.



but the process, on the whole, has given me very satisfactory results, and the possibility of rejecting altogether the use of carbon disulphide is a great gain.

Messrs. Sadtler and Whitfield, remark in their article in *Paving*, "While some of the European asphaltic limestones are capable of being used for paving without addition of fluxing material, they have not been found to make as satisfactory pavement as those containing a siliceous base."<sup>1</sup> Why should they? Is not any form of calcium carbonate easily dissolved by rain-water or decomposed by weak acids, such as abound in the street gutters? Will Mr. Richardson please explain why pulverized limestone is required as an ingredient of the asphalt surface used in Washington? Why is it any better than the same amount of fine quartz sand? The reasons given above are sufficient reasons why it is not as good. In California, infusorial earth occurs in many localities in close proximity to deposits of asphalt. It is found to be a very superior material with which to temper asphalt.

On page 52 of the Report of the California State Mining Bureau, above referred to, an extract appears from the Records of the Standard Asphalt Co. There an attempt is made to compare some of Mr. Richardson's analyses of Trinidad asphalt, made with petroleum ether, with other analyses made by G. Q. Simmons, who analyzed California asphalt by using common ether. Other tests are given, made by H. Stillman, who used presumably petroleum ether from California petroleum. Miss Linton has shown that the solvent powers of these three reagents, when applied to the same asphaltum, vary widely; hence they can not be used interchangeably, and results based upon their use can not be compared. The material used should be petroleum ether of sp. gr. 700 equal to 70° B., obtained from petroleum consisting of hydrocarbons of the marsh-gas series—in other words "paraffins."

These criticisms have not been made at the suggestion of, or in the interest of any party to the asphalt question.

UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.,  
October 30, 1894.

<sup>1</sup> Ibid, September, 1894, 120.

## QUICK ESTIMATION OF STARCH.

By P. L. HIBBARD.

Received November 3, 1894.

THE accurate estimation of starch in presence of crude cellulose or similar substances containing other carbohydrates soluble in hot water or boiling dilute acids, has not yet been accomplished. Lintner's process of heating in closed vessels under high pressure, with water or a weak acid, like tartaric, *e. g.*, is good when soluble convertible carbohydrates other than starch are absent. Märcker's process of dissolving the starch out of the fiber by means of diastase is also fairly satisfactory. But both methods will bring into solution more or less of the various gums, etc., which are nearly always present in starch-bearing material. Entirely to avoid solution of these bodies is, so far, impossible; but it is certain that the less the material is heated with water, or especially with acid, the less will they be dissolved. Perhaps the best method published is Märcker's. The substance is boiled with water a few minutes to gelatinize starch, then cooled to 60° C., some diastase added, and the whole heated on the water-bath at 65° C. for one hour, to hydrolyze the starch. The solution is then filtered from the insoluble residue and converted by hydrochloric acid to dextrose, which is then determined by Fehling's solution. All the directions that I have seen, say the mixture must be heated with diastase for one hour, and then it must be heated two or three hours on a water-bath, with a reflux condenser. A modification of this method consists in heating the substance under pressure of three atmospheres, with lactic or tartaric acid, after the first treatment with diastase. The acid is then neutralized and the whole again warmed with diastase. The conversion to dextrose is as before stated. These methods are somewhat long and tedious, besides being liable to bring into solution other bodies than starch, which, by the subsequent process, will reduce Fehling solution.

Whole corn, soaked a few minutes, was stripped of its hulls. These hulls were carefully examined to see that they were free from starch and were not colored by solution of iodine. After

boiling them a few minutes with water, the solution was filtered off and heated with acid a short time. It then reduced Fehling solution somewhat. This experiment shows that mere boiling with water brought into solution some body, which was converted by acid into a reducing sugar.

Having occasion to estimate starch in residues containing much of other soluble carbohydrates, I have modified the method using diastase, so that it is much shorter and easier, as well as fairly accurate. The method is satisfactory for factory work, where great accuracy is not so necessary as speed; and slightly modified is the most accurate method known.

Instead of taking trouble to prepare diastase by precipitating and washing with alcohol, I make a water extract of malt, which answers well. The coarsely pulverized dry malt is covered with water containing fifteen to twenty per cent. of alcohol. After a few hours the infusion is filtered off and is ready for use. The sugar in this must be determined by treating with acid as described below, in order to make the correction due to it when used to dissolve starch. The alcohol to some extent prevents action of the diastase on the starch of the malt, but is chiefly useful to preserve the malt extract, which would ferment very soon if some antiseptic were not present. Twenty per cent. of alcohol will preserve it for two weeks, even in very warm weather. I have found no effective preservative, except alcohol, that does not destroy the diastatic power of the malt extract.

The substance in which starch is to be determined should be finely pulverized, in order that the starch may be easily extracted without long boiling. Enough of the material to contain at least half a gram of starch is placed in a flask with about fifty cc. of water and one or two cc. of malt extract added. The mixture is at once heated to boiling, with frequent shaking to prevent formation of clots of starch. The addition of diastase before gelatinizing the starch, helps to prevent formation of insoluble clots, as it acts above the temperature at which starch becomes pasty. But if the material contains little starch in presence of much fibrous material, there is no particular gain in adding malt before heating to boiling, as

most of the diastase is destroyed by the high temperature, before it has time to act on the starch. After boiling a minute the mixture is cooled to  $50^{\circ}$ – $60^{\circ}$  C., and two to three cc. malt extract added. Then it is heated slowly from ten to fifteen minutes till boiling, again partially cooled, and tested with iodine solution. If there is blue, the treatment with malt must be repeated. When all the starch is changed, the mixture is cooled, made up to definite volume, and filtered. I have found fine muslin or linen a very satisfactory filter for this purpose. Though it does not at first filter quite so clear as paper, it is more rapid, not being so easily clogged when the substance is albuminous. The cloth retains all the fibrous material, which might give rise to sugar in the subsequent treatment with acid. An aliquot part of the filtrate, sufficient to contain two or three-tenths of a gram of starch, is placed in a 100 cc. flask with five cc. HCl containing thirty per cent. of acid gas, and water to make about sixty cc. total. This is boiled moderately thirty minutes actual boiling, on a sand-bath. This gives complete conversion. I use a sand-bath and no condenser, as the amount evaporated from a narrow-necked flask in this time is not enough to make much difference. If a water-bath is used longer time is required. The solution is now cooled, nearly neutralized with sodium hydroxide, and the dextrose determined by Fehling solution. With pure starch the solutions obtained are almost colorless, but if the substance contains much albuminoid matter, which will be destroyed by the acid, the solution will be brownish. There is no apparent destruction of sugar in this length of time.

The action of various acids on starch has been investigated by F. Salomon, (*J. prakt. Chem.*, **28**, 82,) and it is concluded that hydrochloric is the best acid to use in the hydrolysis of starch. Less than an hour of moderate boiling with the strength of acid above given is sufficient to convert starch directly without previous solution with diastase. Much longer heating destroys sugar and the solution becomes brown.

The residue left after treatment of a good quality of starch by this method is little, but some of it is soluble in dilute acid, so that direct conversion with acid gives a little higher figures, but

it seems probable that this is largely due to other bodies than starch. I have made many experiments to determine the proper time and best strength of solutions, and find the above given most satisfactory.

This method is simple, rapid, and fairly accurate. A determination of starch may be easily finished in less than two hours. Particular points are : prevention of insoluble clots by addition of malt before heating ; the rapid heating prevents any lactic fermentation which may occur in the use of the older published methods ; and the little boiling occasions a minimum solution of bodies other than starch, which could form reducing sugars. With nearly pure starch there is no occasion for use of this method. The process is valuable chiefly for estimating starch in presence of much other material which may give rise to reducing sugars by the action of acid, *e. g.*, fodders, cattle foods, and residues from starch manufacture. A sample of corn hulls, free from starch, gave only a trace of sugar by this method, but direct conversion with acid showed forty per cent. of reducing sugar.

The appended figures show the errors due to the acid method, and afford a comparison of the two :

Material.	Moisture in sample.	PER CENT. STARCH.	
		Malt method.	Acid direct.
Starch factory feed.....	10.0	10.0	40.9
Impure moist starch.....	12.0	81.3	82.3
Impure moist starch.....	...	79.5	80.9
Good starch.....	12.8	84.3	84.6
Purified dried starch.....	...	95.1	96.5
Corn, large white kernels.....	11.0	63.5	68.2
Wheat, hard red variety.....	10.0	60.5	65.0
Bran from same wheat.....	11.3	28.4	44.4
Middlings from same wheat.....	10.1	53.8	60.0
Low flour from same wheat .....	10.2	66.0	67.7
Good flour from same wheat.....	11.0	67.9	69.0
Wheat flour.....	10.0	70.7	73.6
Wheat bran.....	10.1	29.3	46.5

The method may be further improved and each chemist's needs will indicate to him useful modifications. Others may make it more perfect, and to them I commend it as the most promising method for determination of starch.

Most of the careful analytical work in the investigation of the method was done in the laboratory of the University of Nebraska, for the use of which I am indebted to the kindness of Professor H. H. Nicholson.

LABORATORY OF THE ARGO MANUFACTURING COMPANY,  
NEBRASKA CITY, NEB., November 1, 1894.

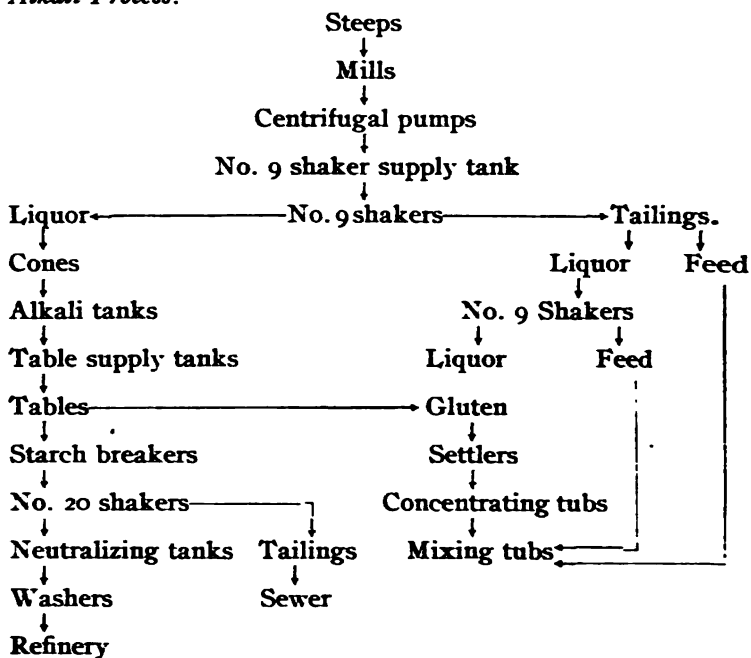
## ALKALI AND SULPHUROUS ACID PROCESSES USED IN THE MANUFACTURE OF STARCH FROM CORN.

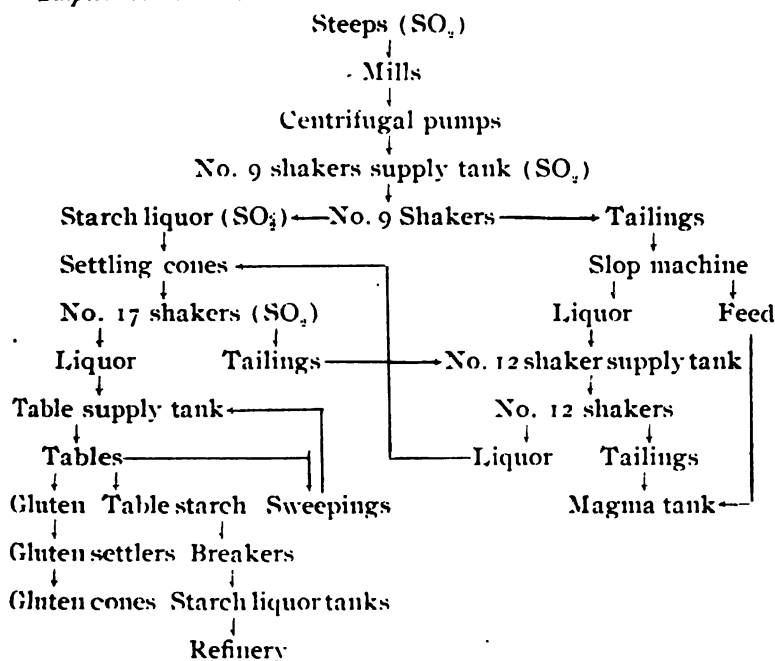
BY HORACE E. HORTON.

Received September 19, 1894.

**S**TARCH is produced from corn at the present time by two processes, known as the alkali and sulphurous acid. I am not aware, at this moment, of the existence of any published article showing the working of these processes, and I take pleasure in presenting two outlines, showing clearly, and at a glance, their essential points.

### *Alkali Process.—*



*Sulphurous Acid Process.*—

I have indicated the points at which the sulphurous acid is added, and will say in this connection, that considerable latitude is allowed. The numbers prefixed to the shakers refer to the number of the bolting cloth used.

TOPEKA, KANSAS, September 12, 1894

## NEW BOOKS.

A TEXT-BOOK OF VOLUMETRIC ANALYSIS, WITH SPECIAL REFERENCE TO THE VOLUMETRIC PROCESSES OF THE PHARMACOPEIA OF THE UNITED STATES. DESIGNED FOR THE USE OF PHARMACISTS AND PHARMACEUTICAL STUDENTS. BY HENRY W. SCHIMPF, PH.G. pp. xviii; 400. 37 Illustrations. New York: John Wiley & Sons. 1894. Price \$2.75.

This book may be considered in the light of a commentary on the Pharmacopeial assay processes. It adheres faithfully to the substance of that work but it is not a mere compilation. To the merit of the author be it said, that the numerous assay direction sprinkled throughout the Pharmacopeia are in his book

classified together systematically, which is by no means an easy task. This has been accomplished by arranging them in the first part of the book, under the following heads: Analysis by Neutralization, Precipitation, Oxidation, Indirect Oxidation (Iodometry), and Analysis of Easily Reducible Substances.

Following a general introduction, accompanied by complete directions for using apparatus, each class is introduced by a clear exposition of its principles, and in addition each assay is treated in a uniformly explicit manner. In some instances other methods are added to those official, as for example, Stolba's method to determine phosphoric acid, Personne's method for valuing potassium iodide, or Kingzett's method to determine the available oxygen in hydrogen dioxide. An excellent feature is, that with each reaction the equation and molecular weights involved are also given, the equivalent weights entering into the percentage calculation being deduced therefrom and stated.

Thus in each assay the operator finds the work a complete guide, nothing being left to conjecture or research, each subject being complete in itself, and hence Part 1st of the book becomes a systematic commentary on the assay methods of the U. S. P.

Part 2nd embraces manipulations of a more elaborate nature, such as the Assay of Opium, Cinchona, Ipecac, The Valuation of Pepsin and of the Resinous Bodies in Jalap and Scammony. These are of great value to pharmacists, and it is to be regretted that in this direction Prof. Schimpf did not enlarge upon the U. S. P. It is needless to state that in such cases gravimetric methods are employed. Attention may be called to the introduction of the methods of Benedict and Sigmundy for estimating glycerol, and of Loewenthal for tannin in barks, these being omitted in the U. S. P., and also to directions for the Volumetric Analysis of Sugar, Urine, Starch in Cereals, Alcohol, Milk, Butter, Fats in Ointments, and numerous others not mentioned in the U. S. P.

Part 3rd is devoted to Gasometric Analysis, and the estimation of Spirit of Nitrous Ether, Hydrogen Dioxide, etc., by the Nitrometer. The Appendix considers Indicators, Reagents, and Test Solutions.

This book is well illustrated and invaluable both to pharma-



cists and to chemists interested in assaying. It is an outgrowth of the Pharmacopeia and the reviewer regrets that space does not permit him to dwell at greater length on its excellent features. Every volumetric method of the Pharmacopeia is recorded explicitly with the one exception for oleic acid in which the process of Muter's Chemistry is substituted, being an improvement, however, in that the assay introduced determines oleic acid in the presence of stearic and palmitic acids which the method of the U. S. P. does not accomplish.

Notwithstanding that such a variety of subjects are embraced and condensed in a comparatively small volume, superficiality can not be charged against it. The book enables the reader, even though he has but a limited training in chemistry, to comprehend and at once carry out each assay described. It should be in the hands of every pharmacist.

J. U. LLOYD.

A TEXT-BOOK OF INORGANIC CHEMISTRY. BY G. S. NEWTH, F.I.C., F.C.S. pp. xiii; 667. 146 Illustrations. London and New York: Longman's, Green & Co. 1894. Price, \$1.75.

To those who have learned to appreciate the value of Newth's "Chemical Lecture Experiments," the announcement of a complete text-book by the same author, will certainly be a matter of interest. Lecturers on experimental chemistry have found the "Experiments" a most helpful guide, replete with clever, ingenious, practical devices for the lecture table, placing at the instructor's service all the latest mechanical and electrical adjuncts, and substituting for many of the antiquated illustrative features, modern striking forms of experimentation.

The same characteristics are to be encountered in the new work, freshness in material and treatment, numerous illustrations, novel and suggestive, replacing many of the time-honored wood-cuts of the standard text-book.

The author's arrangement of matter is a deviation from all the customary methods. He divides his work into three quite distinct parts. Part I—"Introductory Outlines." 150 pages are devoted to theory and chemical physics, notation, nomenclature, atomic weights, valence, heat, pressure, electrolysis, solutions, thermo-chemistry, periodicity, etc. This whole section is

marked by great clearness of presentation and accuracy of statement.

Part II. "The Study of Four Typical Elements." 150 pages are devoted to quite an exhaustive treatment of hydrogen, oxygen, nitrogen, and carbon, with their more important compounds. This section unfrequently recalls Hofmann's famous "Einleitung" where likewise a few elements are utilized to bring out the main essentials of chemical fact and theory. Especially noteworthy in this part is the admirable treatment of *flame* and *combustion* thoroughly up to the times, and far in advance of any existing text-book treatment of these important topics.

Part III. 350 pages are devoted to the remainder of the elements, following closely the periodic classification. The space given each element is necessarily somewhat limited, sodium, for example, receiving but twelve pages, magnesium, four pages, etc. Here we notice, however, as a rule, that the work is well up to the times, notably in technical manufacturing processes. Geographical reference is almost entirely omitted, with some rare exceptions, as in the case of mercury.

Just what is the most advantageous arrangement of the matter in a text-book of this size, is a moot question. Among recent works we find on the one hand Mixer's, adhering rigidly to the periodic classification, and on the other hand Freer's, following the same classification after a study of oxygen, Remsen's doing likewise after a study of oxygen, hydrogen, and chlorine, while, as we have seen, Newth prefaces the same classification with a study of four elements, and prefaces the latter also with an extended section on theoretical and physical chemistry. From my own experience and observation I am inclined to the opinion that the brighter, more persevering students in a college class make satisfactory progress with any of these types, while, on the contrary, a considerable number can profitably take up such a text-book as Newth's only after preliminary drill in some one of the excellent elementary works introducing theoretical concepts gradually, with the acquisition of the necessary experimental facts.

While recognizing fully the many excellent qualities in Dr. Newth's work, attention should be called to several of those

deficiencies which are almost inevitable in an author's first edition. Thus while there is an excellent chapter on thermochemistry in the introduction the subject is almost entirely ignored in the treatment of individual elements and compounds, although in so many cases (as in that of the allotropic forms of phosphorus) it serves admirably to explain important facts.

Uniformity and simplicity in nomenclature are frequently neglected. Note, for example, the following two headings of sections within a few pages of each other: (1) *Arsenuretted Hydrogen* (*Arsenic Trihydride*, *Arsine*), and (2) *Antimony Hydride* (*Antimoniuretted Hydrogen*).

The space assigned individual metals seems frequently too brief; and despite the author's excuse in the preface, I can not approve of the very step-motherly treatment in a book of nearly 700 pages, of the so-called rare metals. Titanium, which is so important to the metallurgist and which forms a larger percentage of our planet than does carbon, receives four lines. Zirconium, cerium, and thorium are passed by with the same meager mention, although their oxides are now in every-day use in our homes for illuminating purposes. This latter fact is omitted entirely, while mention is made of the now much less extended employment of lime for similar purposes. Tungsten, molybdenum, and uranium receive together but one page.

While, as already stated, the work in most instances is quite up to the times—for example, in the account of the lately discovered new element in the atmosphere—still in certain cases there is an inexcusable lack of recognition of recent fact and method.

Thus, under aluminum, we find but a single method of preparing the metal. The historically interesting process of St. Clair Deville receives over a page of description. But not a gram of aluminum is made to-day by that method. That more and more valuable servant of the modern chemist, electrolysis, is granted in fact but scant attention. While a brief allusion to the action of the current on sodium chloride is found in the preface, no mention is made of the important reaction in connection with either chlorine or with sodium compounds. Similarly, while fourteen different methods for preparing oxygen are described in detail, not a word is given to the simplest and most

elegant of all, the reaction between water and sodium peroxide, now employed in every laboratory and lecture-room. No mention is to be found of red fuming nitric acid.

The date of 1876 for Moissan's discovery of free fluorine is probably a typographical error.

T. H. NORTON.

**DIE MASCHINELLEN HILFSMITTEL DER CHEMISCHEN TECHNIK.** von Alwin Parnicke. pp. 320. 327 Illustrations. H. Bechhold, Frankfurt, A. M. 1894.

The lack of a good manual on the methods used for the mechanical preparation of substances used in the chemical industries to which Mr. Pemberton has already called attention in these columns, (see this JOURNAL, 1893, p. 634) is supplied in the excellent digest of the subject contained in this book. The sections into which the book is divided may be translated as follows: 1. Sources of Power. 2. Transmission of Power. 3. Methods of Transportation. 4. Grinding. 5. Mixing. 6. Melting, Dissolving, and Extraction. 7. Concentration. 8. Mechanical Separation. 9. Drying. 10. Weighing, Determination of Temperature, Pressure, and Draught. 11. Laws Relating to the Subject.

The book is well printed and the illustrations are excellent, an important matter in such a book. It is to be hoped the book may find a translator who will condense it sufficiently for class use.

E. H.

**THE ELEMENTARY NATURE OF CHLORINE.** BY HUMPHRY DAVY, SEC. R. S., 1809-1818. PAPERS PUBLISHED IN THE PHILOSOPHICAL TRANSACTIONS. ALEMBIC CLUB REPRINTS, No. 9. 80 pp. Edinburgh: William F. Clay. 1894.

This reprint is no less interesting than its predecessors. The first three papers give the results of experiments made to determine the properties and composition of "muriatic acid." In the remaining six papers Davy describes a few experiments by other chemists and many of his own upon "oxymuriatic acid," discusses them and, without asserting that this gas is an element, suggests that it be called chlorine, on account of its color and because it "is not known to contain oxygen and can not contain muriatic acid." A short account of the discovery and properties of "Euchlorine" is found in one of the papers.

L. B. HALL.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

---

### A MODIFIED ARRANGEMENT OF THE ELEMENTS UNDER THE NATURAL LAW.

BY F. P. VENABLE.

Received December 12, 1894.

A quarter of a century has passed since the first announcement of the Natural Law and the publication of Mendelejeff's table. The truth of the law, in a general way, seemed to be accepted very readily by chemists. It was incorporated in text-books and there explained, but comparatively little use has been made of it in teaching the science. Even Mendelejeff himself, in his *Principles of Chemistry*, has not made the fullest use of it. Victor Meyer, in his lecture before the German Chemical Society more than a year ago, showed how it might be used, and how he used it himself, and, probably, this will do much towards popularizing its use.

There must be some reason why so great a help to scientific study, is not made more use of. Does it lie in a lingering distrust of the law itself or failure to accept it, or is it because of the imperfections in the arrangements of the elements offered by Mendelejeff and others? It is most probably due to the latter, and this paper is presented with the hope of clearing up some of these difficulties.

The modern chemical world has recognized in the discovery of Mendelejeff, the greatest step forward since the announcement of the Atomic Theory. It is too much to expect that so great a discovery should spring full-panoplied from the head of its author.

Doubtless many have observed the imperfections of the law's original form, or rather the table as first given out. Probably some have ventured to comment upon it. Such criticisms have, however, escaped me with one or two exceptions. It is with much hesitation, that I venture to point out what seem to me imperfections and blemishes, in so great a work. Few may agree with me in calling them imperfections. I do not purpose to detract one particle from the greatness and importance of the essential truths contained in this discovery. Mendelejeff's table, as we have it at present, is a great advance upon the first one published by him in 1869, which must be pronounced tentative only, and decidedly unsatisfactory. The table of Victor Meyer is far behind it in presenting the facts of the periodic law. There have been many attempts at devising a graphic representation of this law. I know of none which can be called a real aid to the student, or which do not introduce new ideas which, to say the least, have no basis in the facts as known to us at present. None of them can be regarded as a safe substitute for the simple table of Mendelejeff.

Taking this table I would venture to point out some obstacles to its full acceptance. These have been in part revealed to me by the effort at a presentation of these truths of nature to honest-minded, clear-sighted young men.

Before mentioning the difficulties which lie here in the path of a teacher, I must say, by way of preface, that my criticisms, are aimed at what I may be allowed to call the unessentials of the law. Mendelejeff's great feat was in seeing clearly, and announcing intelligently, that the properties of the elements are dependent upon and determined by the atomic weights. This is the essential of the Natural Law and is in accord with our fullest knowledge. The second part of the law, as usually stated, that these properties are periodic functions, attempts, in a measure, to define the dependence. It may also be true, but it is not fully proved and it is open to objections. It seems to me that this hypothetical portion could well be left in abeyance until fuller knowledge gave it a stronger footing, meanwhile substituting something less open to criticism, and which can not weaken the central truth.

TABLE I.

Group.	I	II	III	IV	V	VI	VII	VIII
Series I	H	—	—	RH <sub>4</sub>	RH <sub>3</sub>	RH <sub>2</sub>	RH	{ Hydrogen compounds.
" 2	Li .	Be .	B .	C .	N .	O .	F .	Fe . Co . Ni . Cu
" 3	Na .	Mg .	Al .	Si .	P .	S .	Cl .	
" 4	K .	Ca .	Sc .	Ti .	V .	Cr .	Mn .	
" 5	(Cu) .	Zn .	Ga .	Ge .	As .	Se .	Br .	
" 6	Rb .	Sr .	Y .	Zr .	Nb .	Mo .	— .	Ru . Rh . Pd . Ag
" 7	(Ag) .	Cd .	In .	Sn .	Sb .	Te .	I .	
" 8	Cs .	Ba .	La .	Ce .	Di? .	— .	— .	
" 9	— .	— .	— .	— .	— .	— .	— .	
" 10	— .	— .	Yb .	— .	Ta .	W .	— .	Os . Ir . Pt . Au
" 11	(Au) .	Hg .	Te .	Pb .	Bi .	— .	— .	
" 12	— .	— .	— .	Th .	— .	U .	— .	
	R <sub>2</sub> O —	R <sub>2</sub> O, RO	R <sub>2</sub> O, —	R <sub>2</sub> O, RO,	R <sub>2</sub> O, —	R <sub>2</sub> O, RO,	R <sub>2</sub> O, —	Higher Oxides. RO,

TABLE II.

Groups.	Higher salt-forming oxides.	Typical, or first small period.	Large periods.				
			1st.	2nd.	3rd.	4th.	5th.
I .....	R <sub>2</sub> O	Li 7	K 39	Rb 85	Cs 133	—	—
II .....	RO	Be 9	Ca 40	Sr 87	Ba 137	—	—
III .....	R <sub>2</sub> O <sub>3</sub>	B 11	Sc 44	Y 89	La 138	Yb 173	—
IV .....	RO <sub>2</sub>	C 12	Ti 48	Zr 90	Ce 140	—	Th 232
V .....	R <sub>2</sub> O <sub>3</sub>	N 14	V 51	Nb 94	—	Ta 182	—
VI .....	RO <sub>2</sub>	O 16	Cr 52	Mo 96	—	W 184	U 240
VII .....	R <sub>2</sub> O <sub>3</sub>	F 19	Mn 55	—	—	—	—
VIII .....	{		Fe 56	Ru 103	—	Os 191	—
			Co 58.5	Rh 104	—	Ir 193	—
			Ni 59	Pd 106	—	Pt 196	—
I .....	R <sub>2</sub> O	H — 1	Cu 63	Ag 108	—	Au 198	—
II .....	RO	Na 23	Zn 65	Cd 112	—	Hg 200	—
III .....	R <sub>2</sub> O <sub>3</sub>	Mg 24	Ga 70	In 113	—	Te 204	—
IV .....	RO <sub>2</sub>	Al 27	Ge 72	Sn 118	—	Pb 206	—
V .....	R <sub>2</sub> O <sub>3</sub>	Si 28	As 75	Sb 120	—	Bi 208	—
VI .....	RO <sub>2</sub>	P 31	Se 79	Te 125	—	—	—
VII .....	R <sub>2</sub> O <sub>3</sub>	S 32	Br 80	I 127	—	—	—
		Cl 35.5			3rd.	4th.	5th.
		2nd small period.		2nd.			



Take the tables from the first volume of Mendelejeff's Principles of Chemistry and examine them. First, we find two kinds of periods made use of—periods containing seven elements, and those containing seventeen. These latter are divided into sevens and threes. If it had only been possible to arrange all of the elements in sevens, as Newlands attempted to do, the periodic idea would have been most convincing, and the Law of Octaves, running through nature, would have seemed most wonderful. But these elements do not admit of being arranged in this way, and the use of periods of different lengths, is to a fresh young mind, unacquainted with mathematical expedients, somewhat forced.

Secondly, there is a very anomalous position assigned to the triads, or as sometimes written, the tetrads, Fe, Co, Ni, Cu, etc. They have been set off to themselves, clearly so as to make the other elements fall, even approximately, into their places, and into the proper sevens. I say approximately, for the student soon sees that although there is a similarity, there is also a wide difference between the elements of the first seven and the last in any period of seventeen.

Thirdly, in the lower periods, in order to get elements to fall into their places, a great many unknown elements have to be interpolated. Thus between cerium and ytterbium, the next element in the list, there are blank places for sixteen elements. The third large period of seventeen has only four known elements in it, and the fifth has only two. That means that here we have a period actually constructed out of fifteen unknown elements and two known ones. This exceeds some of the triumphs of geology in the construction of skeletons of extinct animals. Of the five periods, only one is completely filled out. To say the least, this shows a very imperfect knowledge of the elements, or a great deal of guess work. In the table there are sixty-four known elements and thirty-five blanks for elements yet to be discovered. I hardly think it possible that the majority of chemists, believe that, after all of the diligent search for the past century, less than two-thirds of the elements have been discovered. Where are the others in hiding? Will they be discovered by the spectroscope among the rare earths? There is certainly hope of finding some of them there, but the number which this

• •

statement of the law would require us to find, is simply appalling. The average student thinks, in all honesty, that the coincidences of the first part of the table, will scarcely justify such forcing and wholesale interpolation. If our knowledge of the elements be so imperfect as that, we have no right to force them into periods, in fact, any law based upon their atomic weights would be of the most tentative character, and likely at any time to be overthrown by the discovery of the lost or unknown ones. How do we know that the big one-third, now unknown, may not upset all calculations, when found? Such a law ought rather to be called a working hypothesis. We are venturing a great deal upon a very imperfect knowledge of the ones we have in hand. For if one reckons up the number of elements, for which we have satisfactory determinations of the atomic weights, he will find that they are less than forty. The periodic idea may be true, but we do not know enough about these elements yet, to be able to give this idea a very prominent place in the Natural Law, and we ought to avoid the assumption of so many unknown elements unless it is absolutely necessary.

As I do not intend to tear down without some effort at rebuilding, I would, with much real diffidence, for I realize that I may be looked upon as one who would rush in where only the great masters of the science can safely tread, offer the following suggestions.

The first suggestion is that the wording of the Natural Law be so changed as to read: "The properties of the elements are dependent upon and determined by the atomic weights." The somewhat difficult idea of functions is simplified and periodicity is subordinated. Then the following table might be substituted for the one ordinarily given.

It is not greatly changed and not much originality is claimed for it, but, however slight the changes, I would insist upon their value, because they do away with the dependence upon periods and they certainly make the table easier, more intelligible, and more useful to the student. No very doubtful element is included in it. There is room for additional elements as discovered, but the table is not dependent upon them. Lastly the inter-relation is more clearly brought out.



I do not maintain that this table could ever have been discovered without the idea of periods, though I can see no reason why it might not. The periods still underlie it, but they are out of sight for the present, and are not necessary. The table is not dependent upon them.

The table is constructed as follows. There are seven group elements, having a mean increment of two in their atomic weights. It is by no means essential that there should be just seven of these. At present we do not know more, but I think there is possibly a place for one more, having the atomic weight twenty-one and differing widely from the others as it occupies a singular position.

These group elements are also to be called bridge elements, as they show marked gradation of properties from one to another and serve to bridge over the groups and connect one with the other. Linked to them by an increment of sixteen, are seven typical elements. These show the distinctive properties of the groups to which they belong and a wider divergence from the next group to them. From them can be deduced the properties of the remaining elements of the group. Thus, in group I, Li is the bridge or group element, and Na the type. From this type two lines of elements diverge, averaging three to the line. These triads would, of course, be changed into tetrads or pentads by the discovery of more elements. No importance can be attached to the fact that at present they are triads. There is a distinct increment for each line of elements. These can be averaged thus:

Fig. 1.

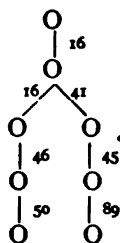


Fig. 2.

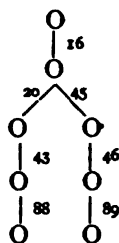


Figure 1 represents the arrangements and increments for the first three groups, and figure 2, that in the last four groups,

the increments showing a variation. These increments could be averaged in all except one case, and the agreements with known atomic weights would be close enough to admit of the easy arrangement of the elements in the prescribed order. Naming the triads right triad and left triad, respectively, we find that these averaged increments would be as follows: The increment from group to type element is sixteen; from type to first element in left triad is eighteen; to second element in left triad is sixty-three; to third element in left triad is 112. On the other side to first element in right triad is forty-four; to second element in right triad is eighty-nine; to third element in right triad is 177.

The one exception mentioned is in the increment from type to third element in right triad, in groups IV to VII. Instead of being 112, the increment here is 141.

To the right of group VII we have three triads which have the regular increments belonging to the left triads, namely, forty-seven and eighty-eight. They are without any type element. It seems most likely that they belong to one group. The group element would have an atomic weight of twenty-one, and the type one of thirty-seven.

The arrangement in the table then, is partly one based upon regular increments in the atomic weights, and, since these weights are but poorly known, partly upon our knowledge of the properties of the elements. When it is recalled that about one-half of the atomic weights are imperfectly known, it will be evident that these averaged increments are approximations only. It is impossible to bring out such perfect symmetry as is obtained in the homologous series in organic chemistry. And yet these groups should be something of the same kind. Following the analogy to the organic hydrocarbons a little further, may not the existence of an element in two different conditions as to valence, etc., as, for instance, copper, or mercury, or iron, be looked upon as a species of isomerism? Such speculations are of little use, however, and quite apart from our present purpose. I have found this table very useful in teaching elementary chemistry, and it can most profitably be made the basis of the entire course. Thus, in the first four groups, the left triads contain

the elements most closely resembling the types. In the last three they are to be found in the right triads. As to natural occurrence of the elements, in the first four groups those in the left triads occur in the same compounds, and generally in connection with the type; those in the right triads occur as the type, or as sulphides, or free. In the last three groups this is reversed. The right triad elements occur as the types, and the left triad elements as the type or as oxides. So, too, the properties of the elements show this relation to the types. Take as an example the specific gravities in group II.

Be = 2.1	
Mg = 1.75	
Ca = 1.5	Zn 6.9
Sr = 2.5	Cd 8.6
Ba = 3.6	Hg 13.6

It is not necessary to pursue this part of the matter at greater length. The careful teacher will easily work out all of these comparisons for himself, and will find that chemistry taught by the table is shorter (so much repetition being saved) and is easier for the pupil, and its symmetry and beauty are much more easily brought out. There is no special claim for originality made here. The germs of such a table, or arrangement, can be found in several text-books, but I do not know of any in which the idea is fully developed, or such a table as this is given.<sup>1</sup> I offer the whole as a suggestion. Perhaps some may find it useful who have met the same difficulties which I have encountered. Others may have overcome these difficulties in a still better way than this. I think, at least, all will agree that there are difficulties, and very serious ones, in the use of Mendelejeff's table, or that of Victor Meyer, as given by their respective authors.

<sup>1</sup> The arrangements of Bayley, Hinrichs, and Wendt are somewhat similar, but the ideas which I would make prominent, are obscured by other considerations and speculations.

## THE DETERMINATION OF POTASH IN KAINITE.

BY RUDOLF DE ROODE.

Received December 12, 1894.

**A**N aqueous solution of kainite contains nothing except potash which, upon evaporation with platinum chloride, forms a compound which is insoluble in alcohol and the ammonium chloride wash ordinarily used in potash determinations. It is, therefore, quite superfluous to precipitate out anything from such a solution by such reagents as barium chloride, ammonium oxalate or carbonate, etc., and to evaporate and ignite the residue obtained. A most accurate result is obtained by evaporating an aliquot portion of a filtered aqueous solution of kainite directly with platinum chloride. Upon the addition of alcohol to the residue obtained by evaporation, nearly to dryness, with platinum chloride, the sodium sulphate present renders the potassium platinochloride sticky and difficult to wash, just as in the Lindo-Gladding method. The sodium sulphate is readily washed out with the ammonium chloride wash, however, leaving a pure potash double salt. The method of direct evaporation of a solution of kainite with platinum chloride has the advantage that there is no loss from occlusion or retaining of potash by precipitates, since no precipitants, such as barium chloride, ammonium oxalate, etc., are used. There can also be no loss from spattering, volatilization, etc., upon ignition, since no ignition is used. Using the same aqueous solution of a sample of kainite, and making determinations by the Lindo-Gladding, the Alternate, and the Stassfurt methods, and also by direct evaporation with platinum chloride, I obtained the following results:

Lindo-Gladding .....	12.36	per cent.	potassium oxide.
Alternate.....	12.42	" "	" "
Stassfurt .....	12.40	" "	" "
Direct evaporation with platinum chloride .....	12.54	" "	" "

AGRICULTURAL EXPERIMENT STATION,  
MORGANTOWN, WEST VIRGINIA,  
December 10, 1894.

## THE OXIDATION OF ORGANIC MATTER AND THE DECOMPOSITION OF AMMONIUM SALTS BY AQUA REGIA, IN LIEU OF IGNITION, IN THE DETERMINATION OF POTASH IN FERTILIZERS.

BY RUDOLF DE ROODE.

Received December 12, 1894.

IN the determination of potash in fertilizers errors may arise, by reason of a loss of potash, when the residue obtained upon evaporation is ignited to destroy organic matter and to drive off salts of ammonium. Such loss may easily occur, either by spattering or a mechanical carrying off of potassium sulphate by the voluminous fumes of sulphuric acid used in the Lindo-Gladding method. In the alternate method, a loss of potash may occur by reason of direct volatilization. Extreme care must be exercised in the ignition, both in the Lindo-Gladding, and in the alternate method, in order to obtain accurate results.

In order to avoid the errors which might arise from such ignition, and, in fact, to do away with the necessity for any ignition whatever, I tried the action of aqua regia. J. Lawrence Smith has shown that salts of ammonium are readily destroyed by aqua regia, and it is well known that organic matter is oxidized thereby. I found, upon evaporating a solution of a mixed fertilizer, prepared as in the Lindo-Gladding method, with nitric and hydrochloric acids, that the salts of ammonium were completely destroyed, and that the organic matter was either entirely destroyed, or else so highly oxidized that it no longer exercised a reducing action upon platinum chloride.

By preparing a suitable solution of a fertilizer and evaporating an aliquot portion of this solution with aqua regia, we ought, therefore, to obtain a residue quite as well adapted to the determination of potash by platinum chloride as a residue obtained by evaporation and ignition.

The *details* of a method for the determination of potash in fertilizers, based upon this principle, have not yet been thoroughly worked out. Some excellent results have been obtained and



some results which were not so good, but, on the whole, the method is quite promising and will be the subject of further study by me, which I trust may result in a somewhat more accurate and more convenient method than those now in general use.

AGRICULTURAL EXPERIMENT STATION,  
MORGANTOWN, WEST VIRGINIA,  
December 10, 1894.

### ON CERTAIN PHENOMENA OBSERVED IN THE PRECIPITATION OF ANTIMONY FROM SOLUTIONS OF POTASSIUM ANTIMONYL TARTRATE.

BY J. H. LONG.

Received December 19, 1894.

I HAVE elsewhere called attention to the behavior of solutions of tartar emetic when treated with solutions of other salts, (see *Am. Jour. Sci. and Arts*, October, 1889 and October, 1890) and with Mr. H. E. Sauer have determined the conditions of precipitation by carbonates, acetates, and phosphates. (*J. Anal. Appl. Chem.*, March, 1891.)

When to solutions of the antimony salt sulphates, chlorides, nitrates, and oxalates of the alkali metals are added no precipitation occurs, even with elevation of temperature. With carbonates, acetates, phosphates, borates, thiosulphates, sulphites, tungstates, and some other compounds, clear solutions can be made at a low temperature, but precipitation follows at a higher point. The precipitate, in nearly all cases, consists of hydrated antimony oxide, and its amount is a function of time, temperature, and amount of added salt.

With mixtures of the tartrate and sodium carbonate, for instance, it was found that in the cold, at the end of twenty-four hours, amounts were precipitated as shown in the following table. In each test five grams of the tartrate were dissolved in sixty cc. of warm water and cooled to 20°. Then different weights of pure sodium carbonate were dissolved in thirty-five cc. of water; these solutions were added to the others and the mixtures were brought up to 100 cc. They were allowed to stand until precipitation was complete, usually over night or longer. An aliquot part of the clear supernatant liquid was

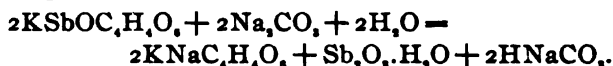
taken and the amount of antimony in solution determined. This was calculated to tartrate in the whole:

No. of experiment.	Na <sub>2</sub> CO <sub>3</sub> added.	KSbOC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·½H <sub>2</sub> O left in solution.
1.....	0.1 gram	99.93 per cent.
2.....	0.3 "	85.22 " "
3.....	0.5 "	70.36 " "
4.....	0.7 "	56.76 " "
5.....	0.9 "	40.87 " "
6.....	1.2 grams	29.17 " "
7.....	1.5 "	13.94 " "
8.....	2.0 "	3.88 " "

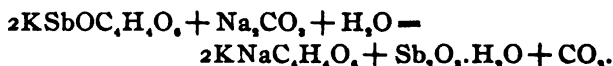
In another series of experiments the solutions of carbonate and tartrate were mixed as before at 20° and then brought to 100°, and maintained at this heat one hour. The precipitates formed immediately, and at the end of the hour were separated by filtration. The filtrates were tested for antimony remaining. The results are shown in the third column below.

No. of experiment.	Na <sub>2</sub> CO <sub>3</sub> added.	KSbOC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ·½H <sub>2</sub> O left in solution.
9.....	0.2 gram	79.23 per cent.
10.....	0.5 "	46.70 " "
11.....	0.8 "	21.74 " "
12.....	1.1 grams	8.69 " "
13.....	1.5 "	6.33 " "
14.....	2.0 "	4.42 " "
15.....	3.5 "	4.66 " "
16.....	5.0 "	4.74 " "

On comparing the two tables, it will be seen that at first the precipitation is much more rapid in hot solution than in cold, but that finally, with excess of carbonate, a more complete decomposition of the tartrate is effected in the cold solution. Two equations can be given, according to which the reaction may take place. The first of these is:



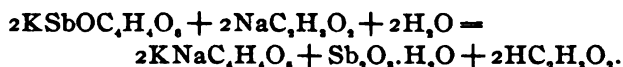
The second is:



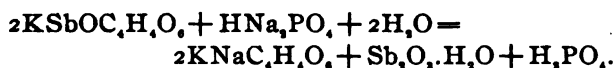
The first, probably, takes place in the cold solution as no carbon dioxide escapes. The loss of carbon dioxide from the hot

solution is less than called for by the equation because an excess of neutral carbonate is present and the solutions are not actually boiled. In any case the precipitation is incomplete, and by addition of increased amounts of sodium carbonate, a condition is reached in which a part of the oxide at first thrown down appears to go into solution again.

Precipitation with sodium acetate takes place imperfectly in the cold, but by heat a stronger reaction follows. In both cases it was found that the results may be expressed by the following equation:



With phosphates the experiments led to the conclusion that precipitation takes place in a manner represented by this equation:



With cold solutions precipitation is very slow, but by heat an amount of the antimony oxide corresponding to seventy-five per cent. of the tartrate originally in solution is obtained.

I have since investigated the behavior of several other salts as precipitants, with the results which follow.

#### REACTION WITH SODIUM BIBORATE.

A very sharp reaction takes place between solutions of borax and tartar emetic, which was studied in the following manner: In the first series of experiments, five grams of the tartrate were dissolved for each test in sixty cc. of water, the solutions being brought to 20°. To these were added definite weights of borax dissolved in thirty to thirty-five cc. of water at the same temperature. The mixtures were made up to 100 cc. exactly, and allowed to stand over night in a place with nearly constant temperature. In all cases a precipitate formed which was separated by filtration. The analysis of the precipitate showed it to have the same composition as that formed by the sodium carbonate; *viz.*,  $\text{Sb}_2\text{O}_3 \cdot \text{aq}$ . On drying at a high temperature most of the water is lost, leaving practically  $\text{Sb}_2\text{O}_3$ .

In each case the precipitate was separated by filtration, and

the filtrate made up to 250 cc. Twenty-five cc. of this was taken and precipitated by hydrogen sulphide, after addition of tartaric and hydrochloric acids in small amount. The precipitation was finished on a hot water-bath, and the precipitate collected on a Gooch filter, washed, dried at 120°, and weighed. The sulphide was calculated to tartrate on the supposition that all the antimony in solution was left in the original form ( $\text{Sb}=120$ ,  $\text{O}=16$ ). The results obtained are shown by these figures:

No. of experiment.	Borax added.	$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ left in solution.
1.....	0.1 gram	98.81 per cent.
2.....	0.2 "	94.74 " "
3.....	0.4 "	87.78 " "
4.....	0.8 "	74.98 " "
5.....	1.6 grams	46.84 " "
6.....	3.2 "	3.31 " "

In another series of tests the solutions containing the borax and tartrate were made up to 250 cc. instead of to 100 cc. They were allowed to stand, filtered, and treated as before, giving these results:

No. of experiment.	Borax added.	$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ left in solution.
7.....	0.1 gram	100.00 per cent.
8.....	0.2 "	97.15 " "
9.....	0.4 "	89.05 " "
10.....	0.8 "	75.29 " "
11.....	1.6 grams	49.09 " "
12.....	3.2 "	6.01 " "
13.....	6.4 "	2.03 " "
14.....	12.8 "	0.99 " "

In a third set of experiments the liquid containing the borax and tartrate was diluted to 100 cc. in a flask, as in the first set. The flask was closed with a perforated rubber stopper having a long glass tube attached, and then heated in boiling water one hour. The liquid was allowed to cool, was filtered, and the filtrate made up to 250 cc. An aliquot part, on analysis, gave results which are shown below.

No. of experiment.	Borax added.	$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ left in solution.
15.....	0.1 gram	99.88 per cent.
16.....	0.2 "	95.37 " "
17.....	0.4 "	88.81 " "
18.....	0.8 "	74.78 " "
19.....	1.6 grams	47.03 " "
20.....	3.2 "	3.96 " "
21.....	6.4 "	1.76 " "

In these tables several things are immediately apparent. It appears that the precipitation is less perfect in hot solution than in cold, although for equal weights of borax the differences are not great. It is seen also that the amounts precipitated are greater in the strongest solutions. These effects of temperature and concentration are far less marked, however, with borax precipitation than with that by the sodium carbonate.

With borax we have, in each case, a very regular rate of precipitation. By plotting the weights of borax in the above table as abscissas, and the amounts of tartrate left as ordinates, we obtain a curve which is almost a straight line.

It seems practically impossible to precipitate all the antimony by excess of borax, although the amount left in solution is much less than when sodium carbonate was used as the precipitant. Direct trials showed that the solubility of the antimonous oxide in excess of borax solution is very slight, but is a trifle greater in the excess of sodium carbonate. The solubility in the Rochelle salt solution formed in the latter case will not account for this difference as will appear below.

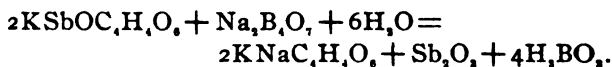
In order to gain further insight into the reaction I measured the amount of rotation of polarized light in a number of solutions before and after the separation of the precipitate of antimonous oxide. Some exceedingly interesting results were obtained, a few of which will be explained in detail. I dissolved five grams of the tartrate in fifty cc. of hot water and added three grams of borax in twenty-five cc. of water, made up to ninety cc., and heated one-half hour in the water-bath. The solution was allowed to cool to 20° and made up to 100.5 cc. (on account of volume of precipitate), and filtered through a dry filter. The filtrate was polarized in a 200 mm. tube, giving

$$\alpha_D = 3.596^\circ.$$

Seventy-five cc. of the filtrate, after the addition of a little hydrochloric and tartaric acids, was precipitated by hydrogen sulphide. The precipitate was collected, washed, and dried in the usual manner in the Gooch funnel. I found 0.119 gram of the sulphide, corresponding to 0.312 gram of  $\text{KSbOC}_2\text{H}_3\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , in the whole filtrate. 4.688 grams had, therefore, been precipitated. From the outset it would naturally occur to one that the

precipitation of antimonous oxide must be accompanied by the formation of sodium potassium tartrate, and that the polarization effect observed must, in part, be due to this, as well as to the potassium antimonyl tartrate left. I have elsewhere given the results of very accurate tests in which the rotation constants of these tartrates were determined by the use of the large Landolt-Lippich polarimeter with the 400 mm. tube (*Am. Jour. Sci. and Arts, loc. cit.*). From these it appears that the rotation of 0.312 gram of the  $\text{KSbOC}_2\text{H}_3\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ , and 3.982 grams of  $\text{KNaC}_2\text{H}_3\text{O}_6 \cdot 4\text{H}_2\text{O}$  (this latter corresponding to the tartar emetic decomposed) in 100 cc. should not be over  $2.6^\circ$ . In the direct polarization of the filtrate I found, as given above,  $3.596^\circ$ . It is evident, therefore, that something else must be present to modify the result.

It is well known that the presence of boric acid increases the rotation of tartrates in a marked degree, and this can be readily accounted for here if we assume that the reaction takes place according to the following equation :



On applying tests for free boric acid its presence was readily shown. We have here apparently a reaction similar to those in which acetic and phosphoric acids are liberated from acetates and phosphates.

In the last experiment it was shown that antimony, corresponding to 0.312 gram of the potassium antimonyl tartrate was still in solution, or that 4.688 grams had been decomposed. To do this according to the above equation would require 2.697 grams of crystallized borax, and would leave in solution 3.982 grams of  $\text{KNaC}_2\text{H}_3\text{O}_6 \cdot 4\text{H}_2\text{O}$  and 1.751 grams of  $\text{H}_3\text{BO}_3$ . An excess of 0.303 gram of borax would be left in solution. To test the correctness of this view I prepared a solution containing in 100 cc., at  $20^\circ$  :

- 0.312 gram of  $\text{KSbOC}_2\text{H}_3\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ .
- 3.982 grams of  $\text{KNaC}_2\text{H}_3\text{O}_6 \cdot 4\text{H}_2\text{O}$ .
- 1.751 grams of  $\text{H}_3\text{BO}_3$ .
- 0.303 gram of  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ .

This solution was polarized in the 200 mm. tube and gave

$$\alpha_D = 3.590^\circ,$$

which agrees very well with the result of the first experiment.

Another solution, containing in 100 cc., at  $20^\circ$ ,

0.150 gram of  $\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ ,

4.119 grams of  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ,

1.811 grams of  $\text{H}_3\text{BO}_3$ ,

gave  $\alpha_D = 3.661^\circ$ . While boric acid increases the rotation of tartrates and tartaric acid I have elsewhere shown that borax decreases the rotation of Rochelle salt slightly. The equation probably represents the facts properly.

In the above nothing has been said about certain peculiarities observed in the formation of the precipitates. When cold dilute solutions of borax and the tartrate are mixed no reaction takes place immediately, but with warm, strong solutions, a precipitate seems to form as soon as the two liquids are poured together. In a former paper (*J. Anal. Appl. Chem., loc. cit.*) I pointed out the important and exceedingly curious fact that in the reaction between carbonates or acetates on the one hand, with the tartrate on the other, while no precipitate may appear immediately, perhaps not in hours, indicating a decomposition, the polarimeter shows that such has taken place. Here, also, we have evidence that a reaction has taken place even without precipitation, and this the polarimeter furnishes. The matter can be best explained by giving the details of several experiments.

I made five solutions by dissolving five grams of the tartrate as before in fifty-five to sixty cc. of warm water, cooled to  $20^\circ$ , and added certain weights of borax in small volumes of water, making the solutions finally to 100 cc. at  $20^\circ$ . These solutions were polarized immediately in the 200 mm. tube, with the following results:

No. of experiment.	$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ taken.	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ added.	$\alpha_D$
1.....	5 grams	0.5 gram	12.08°
2.....	5 "	1.0 "	9.40°
3.....	5 "	2.0 grams	5.53°
4.....	5 "	3.0 "	4.10°
5.....	5 "	4.0 "	3.75°

The normal rotation of the tartrate at  $20^{\circ}$  in the 200 mm. tube, with a concentration of five grams in 100 cc., I have shown to be

$$\alpha_D = 14.103^{\circ}.$$

The effect of the borax is therefore marked, but the extent of the decrease in rotation depends on the number of minutes intervening between the mixing of the solutions and the completion of the observation in the polarimeter. A gradual decrease in the readings was in all cases observed, until the solutions became finally too turbid for observation from the beginning precipitation. The first solution, for instance, in the above table was read as follows:

10 hours, 30 minutes,	$\alpha_D = 12.08^{\circ}$
10 " 45 " "	$= 11.87^{\circ}$
10 " 55 " "	$= 11.80^{\circ}$

After standing some hours, the solutions deposited a precipitate and cleared up. On again polarizing I found:

No.	$\alpha_D$
1.....	$11.52^{\circ}$
2.....	$9.01^{\circ}$
3.....	$5.29^{\circ}$
4.....	$3.92^{\circ}$
5.....	$3.65^{\circ}$

These observations were made in a 200 mm. tube, but similar solutions were polarized in a 400 mm. tube with perfect sharpness, the readings agreeing within  $0.02^{\circ}$ , as is possible with the large and excellent instrument used. I mention this to prove the perfect transparency of the liquids, and to show that the decreased rotations observed at the start were not due to any loss through precipitation, but were in consequence of changes preceding precipitation, these changes taking place very gradually.

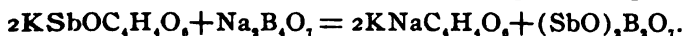
We have here a phenomenon reminding one of the birotation of solutions of certain sugars, but depending on a different cause undoubtedly. In the reaction between the same tartrate and sodium carbonate the same change was observed, but through a longer period. A solution containing in 100 cc. one-tenth gram of the carbonate and five grams of the tartrate gave, at the end of five minutes in a 400 mm. tube, a rotation of  $25.582^{\circ}$ , after



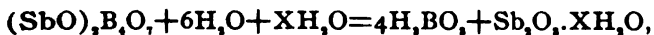
thirty minutes,  $25.580^\circ$ , that is, practically the same, but after twelve hours,  $24.480^\circ$ . A perfectly clear mixture can be made containing five grams of the tartrate and nine-tenths gram of sodium carbonate in 100 cc. When polarized immediately, I found with this in the 400 mm. tube  $\alpha_D = 11.57^\circ$ , after ten minutes,  $11.50^\circ$ , after twenty-five minutes,  $11.132^\circ$ , and after sixty-five minutes,  $10.55^\circ$ .

In the normal reaction between carbonates or borates and the potassium antimonyl tartrate a precipitate should be formed, but we find that at a low temperature this is much delayed. If precipitation alone were taken as the indication of a reaction it would necessarily appear that at the outset no reaction takes place, but the behavior with polarized light shows the error in this view. It is evident that a reaction begins immediately and progresses far toward completion in some of the cases considered before even the first polarization can be made, that is within two or three minutes. This first part of the reaction is the beginning stage of precipitation and may consist in the formation of some intermediate product, which finally decomposes. I have elsewhere shown (*Am. Jour. Sci. and Arts, loc. cit.*) that the rotation of potassium sodium tartrate is decreased by the addition of sodium, thallium, and lithium salts, but is increased by the addition of potassium and ammonium salts and that this reaction is fully accounted for if we assume the formation of sodium tartrate, sodium thallium tartrate or sodium lithium tartrate in the one case or of potassium or potassium ammonium tartrate in the other. In the present instance we evidently must admit the formation of sodium potassium tartrate from the instant the solutions are mixed, but that the reaction is a progressive one. The potassium antimonyl compound with a high rotation gives place to the potassium sodium compound with a much lower rotation. There is nothing to show, however, in what form the antimony is held.

Possibly the reaction may be explained by assuming the formation of an intermediate product according to this equation:



If the last compound is formed it must break up in this manner:



leaving a hydrated oxide of antimony with more water than the final precipitate contains. By loss of water, possibly, this hydrated compound must, in time, settle out as a precipitate. It has been explained that by boiling, the precipitate forms and subsides soon. At  $20^{\circ}$ , even after what I have called the preliminary stage of precipitation, may have occupied hours, the actual formation of the precipitate may consume an equally long time. The precipitate is a growth through an invisible and a visible stage, and what is true here is true of the next case to be given.

#### REACTION WITH SODIUM TUNGSTATE.

Cold solutions of the tartrate give no immediate precipitate when mixed with cold solutions of ordinary sodium tungstate, but on standing the mixtures gradually become turbid and finally deposit a sediment. The composition of this depends largely on the temperature and concentration. The precipitate formed in the cold, collected and dried at  $105^{\circ}$ – $110^{\circ}$  C. consists, essentially of antimony oxide. A precipitate formed by mixing hot solutions has practically the same composition, but if obtained after long heating it contains a relatively larger amount of tungstic acid.

In a series of tests made by mixing hot solutions of the two salts, and allowing the mixtures to stand several hours to cool, the following results were obtained :

$\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ in 100 cc.	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in 50 cc.	Wt. of ppt.	$\text{Sb}_2\text{S}_3$ from same.	Per cent. of Sb. in ppt.
1 gram	2 grams	0.3087	0.3467	80.22
2 grams	2 "	0.6442	0.7291	80.84
4 "	2 "	0.5728	0.6486	80.88
5 "	2 "	0.7222	0.8170	80.79

The mixtures were made in platinum dishes holding about 200 cc., and as the precipitates formed as a coherent coating on the dishes they were easily washed, dried at  $110^{\circ}$ , and weighed. They were then dissolved in diluted hydrochloric acid, which left a small amount of tungstic acid in each case in flocculent form. The solutions were then filtered, and, after the addition of some tartaric acid, were precipitated by hydrogen sulphide in the usual manner. The sulphide precipitates were collected on a Gooch, dried at  $110^{\circ}$ , and weighed. It will be seen that the

results are a little low to correspond to pure antimony oxide as the composition of the white precipitate. This compound contains 83.3 per cent. of antimony. The compound  $\text{Sb}_2\text{O}_3 \cdot \text{H}_2\text{O}$  contains 78.4 per cent. The lower results are doubtless due to the small amounts of tungstic acid left in each case on treatment with hydrochloric acid, and referred to above.

In a second series of experiments constant amounts of the tartrate in hot solution were mixed with varying amounts of the tungstate likewise in hot solution. The white precipitates which formed were collected and weighed as before, with the following results, which show the effect of excess of tungstate on the amount of precipitate. In each case two grams of the tartrate was taken in 100 cc., and the tungstate in fifty cc.:

Tungstate taken.	Ppt. obtained.
0.5 gram	0.1070
1.0 "	0.4598
2.0 grams	0.5762
3.0 "	0.5861
4.0 "	0.6143
5.0 "	0.6185

From this, it is plain that the amount of precipitate is not much increased by great excess of the tungstate beyond a certain point. In the cold, precipitation is much less perfect, while, by boiling, fully three-fourths of the theoretical yield of oxide from the tartrate can be obtained.

By working with cold solutions a mixture may be made which remains clear long enough to permit polarimeter observations to be taken. I dissolved five grams of the tartrate in sixty cc. of water, cooled to  $20^\circ$ , and added five-tenths gram of the tungstate in twenty cc. of water. The mixture was made up quickly to 100 cc. at  $20^\circ$  and polarized in the 200 mm. tube immediately and after intervals of five minutes. I found without refilling the tube:

1st observation	$\alpha_p = 11.66^\circ$
2nd "	" = $12.03^\circ$
3rd "	" = $12.13^\circ$
4th "	" = $12.53^\circ$

The solution became now too turbid, from separation of a precipitate. for further tests. On standing some hours the remainder

of the solution in the flask cleared after subsidence of its precipitate. A portion of this examined gave

$$\alpha_D = 12.74^\circ.$$

Another portion of the same solution, heated and then cooled to  $20^\circ$ , gave the same. A new solution prepared in the same manner gave, after standing some time,

$$\alpha_D = 13.11^\circ.$$

I made next a solution containing in 100 cc. five grams of the tartrate and one gram of the tungstate. This examined, immediately, at  $20^\circ$ , gave

$$\alpha_D = 9.42^\circ,$$

but it soon became turbid and deposited a precipitate. After clearing, I found

$$\alpha_D = 11.48^\circ,$$

which increased to  $11.87^\circ$  by heating the liquid.

These reactions are especially interesting when compared with those between the tartrates and other salts. We have here, as before, a marked decrease in the specific rotation on mixing the solutions of the active and inactive substances. But in the case of the tungstate on standing, there is an increase instead of a decrease in the rotation observed in the other cases. This behavior finds its explanation probably in the action of the liberated tungstic acid. The reaction between the two salts undoubtedly follows this equation :



The precipitation of the tungstic acid is very slow and incomplete. While in solution, it may combine with the soluble tartrate to form a body with increased rotation, the possibility of which is shown by the researches of Gernez and others. The delay in the appearance of the precipitate may be due to the formation and slow breaking up of intermediate products containing the antimony and tungstic oxides in temporarily soluble condition. With liberation of the tungstic acid we have a gradual increase in the already decreased rotation. This change in the rotation, before precipitation, is well shown in the following observations. I dissolved five grams of the tartrate and two and five-tenths grams of the tungstate, mixed at a low tempera-

ture and made up to 100 cc. as before, and at exactly 20° C. A reading with the 200 mm. tube was made as soon as possible and, without changing the solution, this was repeated at frequent intervals. The results were as follows :

3 hours, 28 min.	$\alpha_D = 5.66^\circ$
"	" = $5.96^\circ$
"	" = $6.45^\circ$
"	" = $6.83^\circ$
"	" = $7.15^\circ$
"	" = $7.32^\circ$
3 hours, 44 min.	" = $7.43^\circ$
3 hours, 58 min.	" = $7.90^\circ$

At this point the liquid began to grow slightly turbid, so that the observations could not be continued. The remainder of the liquid was then heated in a closed flask to complete the precipitation, cooled to 20°, and tested. I found now

$$\alpha_D = 9.13^\circ.$$

The liquid still remaining was filtered, fifty cc. of the filtrate taken and precipitated with hydrogen sulphide, yielding finally 0.4045 gram of antimony sulphide. From this it appears that of the tartrate originally taken, 1.599 grams remained in solution in the 100 cc. (no allowance being made for the volume of the precipitate).

From this we have

$\text{KSbOC}_2\text{H}_3\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$	decomposed	=	3.401	grams.
"	"	remaining	1.599	"
$\text{KNaC}_2\text{H}_3\text{O}_6 \cdot 4\text{H}_2\text{O}$	formed		2.888	"

Now, the rotation corresponding to the tartar emetic remaining is  $4.50^\circ$  and that to the Rochelle salt formed is  $1.25^\circ$  from which we should expect a total rotation of  $5.75^\circ$ . This, in fact, corresponds very nearly to what was observed at the beginning of the test, and seems to bear out the suggestion made above: *viz.*, that the principal reaction here occurs before actual precipitation appears. A splitting of the tartar emetic is indicated by the immediate decrease in the rotation and then the complex effect of addition of the liberated tungstic acid to the alkali tartrate in solution appears from the gradually increased rotation

Precipitation finally follows as the end of the reaction; the separated part assumes the insoluble form.

It will be recognized that the phenomenon in this case is much more complex than in the other. There is nothing to show that while the rotation is being increased by the action of the tungstic acid there is not also a tendency toward decrease because of progressive decomposition of the potassium antimonyl tartrate. In all probability the observed rotation is a resultant effect.

#### REACTION WITH SODIUM THIOSULPHATE.

Cold dilute solutions of the thiosulphate and potassium antimonyl tartrate can be mixed without immediate precipitation. Application of heat, however, produces a light yellow precipitate which grows deeper and finally becomes bright red. This precipitate is the substance commonly known as antimony cinabar, used as a pigment, and on the large scale is made by decomposing the thiosulphate by antimony chloride. In the reaction between the thiosulphate and tartar emetic the precipitate appears very heavy, but the decomposition is far from complete as shown by the figures given below.

There seems to be some doubt as to the composition of this precipitate. Roscoe and Schorlemmer (2, part 2, 324) give it as, probably,  $\text{Sb}_2\text{S}_3\text{O}$ , referring, however, to other formulas. Dammer's Handbuch gives  $\text{Sb}_2\text{O}_3 \cdot \text{Sb}_2\text{S}_3$  as the probable formula. Others are also given. Recently Baubigny (*Compt. rend.*, No. 17, 1894), has given reasons why the formula  $\text{Sb}_2\text{S}_3$  should be considered the correct one and the proof he presents appears to be satisfactory. There remains a possibility, however, that the composition may, under certain circumstances, vary with the method of preparation. In fact, some of my own results seem to show this and I am now engaged in studying the question further. But as made in the reaction in hand the composition seems to be  $2\text{Sb}_2\text{S}_3 \cdot \text{H}_2\text{O}$ . This was determined by the following considerations: The precipitate dissolves in hydrochloric acid without liberation of sulphur, yielding a perfectly clear solution. A solution made in this way was heated, mixed with a little tartaric acid solution, and precipitated by hydrogen sulphide in the usual manner. On filtering off the orange-yellow precipi-

tate so obtained in a Gooch crucible, drying at  $120^{\circ}$ , and weighing, the weight was always found less than that of the antimony cinnabar taken.

Sulphur determinations were made by dissolving a gram or less of the substance in strong S-free solution of potassium hydroxide and then oxidizing the sulpho-salt formed by washed chlorine gas, (method of Rivot). The results of these tests were as follows:

	Calculated for $2Sb_2S_3 \cdot H_2O$ .	Found.
Sb.....	69.56	69.80
S.....	27.83	27.72

No determination of the water was made, but its presence was shown in the substance dried at  $120^{\circ}$  by heating to a higher temperature in a narrow glass tube.

In a series of experiments on the precipitation a number of portions of the tartrate, of five grams each, were weighed out and dissolved in 150 cc. of water. Varying amounts of the thiosulphate in fifty cc. of water were added and then water enough to make exactly 250 cc. The flasks holding the mixtures were closed with perforated stoppers containing long glass tubes and then heated in the water-bath one hour. In this way evaporation was practically avoided. At the end of the hour the precipitates were collected on a Gooch funnel, dried at  $120^{\circ}$ , and weighed with the following results:

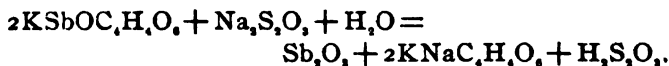
No. of experi- ment.	Weight of $Na_2S_2O_3 \cdot 5H_2O$ added.	Weight of precipitate.
1.....	0.1 gram.	0.0039 gram.
2.....	0.2 "	0.0068 "
3.....	0.4 "	0.0111 "
4.....	0.8 "	0.0178 "
5.....	1.6 grams.	0.0363 "
6.....	3.2 "	0.0803 "
7.....	6.4 "	0.2112 "
8.....	12.8 "	0.4809 "

In a second set of tests I dissolved, in each case, ten grams of the tartar emetic in 100 cc. of hot water and added the thiosulphate in fifty cc. of hot water. The mixtures were kept at  $100^{\circ}$  two hours and then filtered. Results as follows:

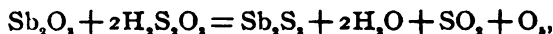
No. of experiment.	Weight of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ added.	Weight of precipitate.
9.....	5 grams.	0.1915
10.....	10 "	0.4041
11.....	15 "	0.5162
12.....	20 "	0.6818

It is evident from these figures that in both sets of experiments the reaction is far from complete and not easily determined. It is, perhaps, quite complex. I noticed in no case the escape of hydrogen sulphide or sulphurous oxide and the gradual change in color during precipitation from very light yellow to bright red suggests that it takes place in two stages. Vortmann (*Ber. d. chem. Ges.*, **22**, 2307) has studied the general problem of decomposition of thiosulphuric acid and states that it breaks up into  $\text{H}_2\text{S}$ ,  $\text{O}$ , and  $\text{SO}_2$ . In presence of certain metals, tetra- and pentathionates seem to be formed. It is certain that no sulphate is formed in the reaction in hand, but the proof of formation of the several thionic acids is difficult because of the incompleteness of the reaction and the presence of the great excess of thio-sulphate. In cases of complete reaction, however, Vortmann and Vaubel, also, (*Ber. d. chem. Ges.*, **22**, 2703) have shown that these acids are formed.

I suggest, therefore, this explanation of the present reaction. At the outset there may be, as with borax, a decomposition according to this equation,



then



the oxygen and sulphur dioxide being held, however, to form polythionates.

The gradual change of color can be accounted for by the gradual change of oxide into sulphide of antimony and it seems possible that under certain conditions of concentration and temperature a part of the oxide should remain unchanged, accounting for the results of some of the analysts who have examined the precipitate. In several instances I modified the experiment by mixing warm solutions of the tartar emetic with warm thio-sulphate solutions, and then throwing the mixture into a large



volume of cold water the instant a precipitate began to form, to check the reaction. The precipitate which now settled was very light colored instead of red, and appeared to be a mixture of oxide and sulphide. The microscopic appearance of this precipitate is distinctly different from that of the antimony cinnabar.

As explained at the outset some time elapses after mixing cold solutions before a precipitate appears. In the beginning of the interval the solution may be so clear that accurate polarimetric observations are possible. But, contrary to expectations, based on the behavior in other cases recorded, I find the specific rotation of the tartar emetic, in this stage of the reaction, quite unchanged. After precipitation a marked decrease was observed as usual. This is shown in the following table in which the filtrates from the last precipitates referred to were made up to 250 cc. before polarization:

No. of experiment.	Thiosulphate added.	$\alpha_D$ observed.	$\alpha_D$ calculated.
9.....	5 grams.	10.90°	10.89°
10.....	10 "	10.43°	10.46°
11.....	15 "	10.07°	10.24°
12.....	20 "	9.69°	9.93°

In the last column the rotations were calculated on the assumption that antimony is precipitated and Rochelle salt formed according to the last equations. In the eleventh and twelfth experiments the thiosulphate is present in amount much in excess of that necessary to complete precipitation by these reactions, and it is evident that a decomposition of the active molecule has taken place not indicated by the amount of precipitate.

There seems to be a fundamental difference between the reaction with the thiosulphate on the one hand, and those with the borate, carbonate, phosphate, acetate, and tungstate on the other. In the first case we appear to have no breaking up of the complex tartrate until actual precipitation occurs, while in the others the stages are quite distinct. I have shown that in these last reactions acids are liberated which may be readily recognized. It is also true that these acids are practically without action on antimonous oxide, from which it would follow that this substance might remain a long time, possibly in the

hydrated form, in contact with the liberated acids without change. This would not be the case with liberated thiosulphuric acid. If set free in the presence of antimonous oxide, even the dry precipitate, it soon converts it into sulphide. Any cause, therefore, which acts to destroy the equilibrium in the solution of tartrate and thiosulphate must lead to the almost immediate formation of a precipitate.

In many of our most familiar cases of precipitation the formation of the precipitate is so rapid that we are accustomed to look upon it as instantaneous. But by varying the conditions of precipitation it may be shown that even the reaction between barium chloride and sulphuric acid is one which consumes an appreciable interval. In such cases, however, we have no means of knowing what takes place before the precipitate becomes actually visible. It is, doubtless, true that the liquid regarded as supersaturated for  $\text{BaSO}_4$  does not begin to throw this out in solid form until a relatively large number of these molecules combine to produce a particle of a certain size, but at what rate the Ba and  $\text{SO}_4$  ions combine can not be shown.

But in the cases before us we have evidence, first, of the gradual breaking up of the complex potassium antimonyl tartrate and then, also, that a relatively large amount of the antimony may be separated before any of it falls as a precipitate. The stage of precipitation seems to follow as a perfectly distinct and also progressive one. It is hastened, as in other cases of supersaturation, by heat or agitation. One of the reactions shows, also, that a relatively long time is consumed in combination as well as in dissociation. In the case of the mixture containing the tartrate and tungstate we have evidence of the splitting of the first molecule, and then, from the slowly increasing rotation, evidence of the addition of an element from the second to the active part of the first. Both of these phenomena are observed before precipitation appears.

It must be remembered that the several acids shown to be liberated in these experiments are all so-called weak acids, or acids but slightly dissociated in solutions. It is also true, as a test of their electric conductivities shows, that the solutions of tartar emetic are relatively little dissociated (see in this connec-

tion Hugo Haedrich, *Ztschr. phys. Chem.*, 12, 496). There is doubtless, therefore, a close connection between the phenomena outlined above, and others depending on the degree of dissociation of the ions in solution. A study of the behavior of weaker solutions would doubtless lead to interesting results not brought out in the above experiments which were undertaken mainly to show the character and amount of precipitates formed. A discussion of the behavior of dilute solutions will follow.

CHICAGO, December, 1894.

---

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE  
SCHOOL OF APPLIED SCIENCE. XXI.]

## AN EXAMINATION OF THE ATMOSPHERE OF A LARGE MANUFACTURING CITY.<sup>1</sup>

BY CHARLES F. MABERY.

Received December 13, 1894.

THE composition of the atmosphere was determined in the latter part of the last century by the classic researches of Priestley, Cavendish, Lavoisier, and others. These investigations were stimulated by Priestley's discovery of oxygen and the discovery of nitrogen by Rutherford. The proportion of nitrogen was first ascertained by Cavendish, and the precise quantitative composition was ascertained by Lavoisier, who repeated the celebrated experiment of Priestley, in which metallic mercury was heated for a long time in a confined volume of air to determine the quantity of gas absorbed and the residual nitrogen. The composition of the atmosphere with reference to the proportion of oxygen and nitrogen has since been frequently determined without showing any appreciable variation. In specimens of air collected from regions widely separated, Morley (*Am. Chem. J.*, 2, 276) determined with the utmost precision the proportion of oxygen and nitrogen without finding any appreciable variation.

The essential constituents of the atmosphere include oxygen, nitrogen, and carbon dioxide in constant proportions, nitrous and nitric acids, sulphurous and sulphuric acids, dust, soot, moisture, ammonia, and certain other constituents in variable

<sup>1</sup>The experimental work of this paper was performed under my direction by Mr. Charles G. Snyder, and it formed the subject of his thesis for the Degree of Bachelor of Science.

proportions depending upon atmospheric conditions and local influences. The allotropic form of oxygen, ozone, is an important constituent of the atmosphere, and probably also hydrogen dioxide.

With a population distributed over large areas, natural conditions are sufficient to keep the atmosphere in a normal and healthful condition for the support of life. Such has been the condition in all civilized countries until within the last thirty years the rapid accumulation of population near manufacturing centers and in cities, and the enormous consumption and incidental waste of coal has introduced important changes at these points. Not only are manufactories and other large establishments dependent for their maintenance upon the consumption of coal, but private habitations, which were formerly heated with wood as fuel with the production of a harmless smoke, now depend almost entirely upon coal. If hard coal is burned the smoke is not objectionable, but the escape of bituminous coal smoke from every household chimney in a densely populated city, together with dense volumes poured forth from large blocks is sufficient to keep the atmosphere in a questionable condition in relation to health, comfort, and the deleterious effects on perishable forms of property. Under occasional conditions of strong winds or rain, followed by clear weather, the city atmosphere is doubtless in a harmless condition; but it can not long remain unpolluted with immense volumes of sooty smoke poured forth from many chimneys.

Abroad, especially in England, the atmosphere of large cities, notably in manufacturing towns, has received considerable attention. Doubtless, on account of the rapid growth of American cities, and probably, also, because of an abundant supply of anthracite coal for cities too far removed from the regions of bituminous coal to render it profitable, the atmosphere of our cities has received little attention. But for cities situated near the soft coal regions, the question of atmospheric pollution has become of too serious moment to be long disregarded.

To understand the nature of smoke pollution it is necessary to refer to the composition of coal and to the products of its combustion under different conditions. Bituminous coal consists

principally of compounds of carbon and hydrogen, or hydrocarbons with smaller proportions of nitrogen and sulphur compounds, and metallic compounds known as the ash when the coal is burned. So far as atmospheric pollution by coal smoke is concerned, the four elements, carbon, hydrogen, sulphur, and nitrogen, are the only constituents of coal that need to be considered.

In the combustion of coal with an adequate supply of air, under such conditions that the chemical reactions involved can be completed within the space allotted to combustion, the ultimate products are carbon dioxide, carbon monoxide, water, sulphurous acid, and ammonia. The less carbon monoxide the smoke contains the more efficient is the combustion; the sulphurous acid is usually converted, at least in part, into sulphuric acid by further oxidation in presence of moisture. It is only rarely, however, that the conditions requisite for complete combustion are maintained. The following features will be recognized as having an important bearing upon the question of complete combustion: (1) A sufficient supply of air; (2) the combustion should not be forced too rapidly; (3) the temperature, especially at the moment of firing, must not be too low; (4) the size, form, and proportions of the space within which the combustion takes place must be suitably adapted. These are the principal points with which complete combustion is concerned, and they are evidently closely connected with the manner of firing and general care of the heating apparatus. In practice, these conditions are far from being realized; with an insufficient supply of air unequally distributed with reference to the fuel, especially with a low temperature, the carbon is only partially burned and the portion not consumed escapes in the form of soot.

The hydrogen burns first, and it has an important influence in maintaining the temperature sufficiently high for complete combustion of the carbon. If the coal contain considerable sulphur it must escape as sulphurous acid, or as sulphuric acid in complete combustion, or (as hydrogen sulphide) in incomplete combustion, and it would seem to be impossible to avoid deleterious effects of these acids in the atmosphere. No doubt sul-

phuric acid should have some effect on such materials as book-bindings and delicate fabrics after collecting in dust during long periods of time, but the effect is greatly increased by the presence of soot, which, as we shall show, absorbs the acid, and when it collects on any surface it occasions a greater accumulation of the acid than should occur in its absence.

The state of the atmosphere in cities where bituminous coal is the principal fuel is dependent upon conditions of combustion in which the chemical reactions are far from complete, with the result that the carbon escapes from the chimney in part as carbon dioxide, in part as carbon monoxide, and in a considerable part as soot. Under such conditions the sulphur is set free as a mixture of sulphuric and sulphurous acids and hydrogen sulphide. The latter is readily shown by its effects on metals, especially on silver, which soon becomes badly discolored on account of the formation of argentic sulphide. The soot ordinarily present in the atmosphere has a greasy consistency, readily recognized by subjecting it to pressure. It consists to a considerable extent of compounds of carbon and hydrogen known as hydrocarbons, which escape from the coal by a process of destructive distillation under conditions somewhat similar to those in the distillation of coal in gas retorts. As mentioned above it carries with it the sulphur acids and ammonia, and it is highly destructive to vegetable life, its action depending probably in part upon the formation on the leaves and stems of a thin layer of tarry substance, which clogs the pores, thus interfering with the process of plant respiration. Sulphuric acid is highly destructive to the forms of organic compounds of which vegetation is composed and in soot it may accumulate to such an extent as to be injurious.

In complete combustion with no escape of soot, even on a very large scale, as in manufactories, it is safe to assert that the natural conditions of the atmosphere may prevent any undesirable effect from the products given off.

During the year 1889 the quantity of coal consumed in Cleveland included 117,157 tons of anthracite and 924,602 tons of bituminous coal. Assuming one per cent. of sulphur in the latter, which is the average composition, 9,246 tons of sulphur

were evolved in the combustion of the soft coal, equivalent to 28,305 tons of sulphuric acid, or nearly eighty tons a day. Without doubt this acid is ultimately neutralized in the atmosphere with the formation of ammonium or sodium salts, but directly it is sent forth it must exist chiefly as the free acid. In the evolution of considerable quantities of sulphur no doubt a portion remains for some time in the atmosphere in the form of sulphurous acid. In the city of Lille, France, as much as two cubic centimeters of sulphurous acid per liter has been found in the atmosphere and the rain water collected contained 0.022 gram per liter.

The ammonia evolved in the combustion of coal is not harmful. Indeed in combination with acids it is a normal constituent of the atmosphere. As one of the ultimate products of the decay of vegetable and animal bodies it is continually set free in this manner and it forms an essential element in the food of plants. The cycle of changes includes the evolution of nitrogen as ammonia from decaying organic bodies and the reabsorption as food by plants from the soils which receive it with the rain. Ordinarily natural conditions are sufficient to complete the transformation of the organic compounds during decay into ammonia in an equal distribution such as exists in the economy of nature. But when accumulation of animal or vegetable organic matter occurs at certain points, as in cities, the oxidizing forces of the atmosphere may not be sufficient to accomplish the vast amount of labor involved in decomposition and purification. On account of the extreme instability of the nitrogenous organic compounds these decompositions take place with great readiness in a limited supply of air but with the evolution of products that are a dangerous pollution in the atmosphere. The evidence of such changes in cities is not far to seek, especially if sanitary regulations are not rigidly enforced. Every stable, imperfect sewer connection, cesspool, sink drain, or offal receptacle readily contributes its share to the atmospheric pollution.

In chemical analysis the nitrogen in such products of decay is evolved as ammonia, and from its source in albumen and allied bodies it is known as albuminoid ammonia. Its presence in water or in the atmosphere may be accurately determined and it

may indicate a dangerous condition since its formation is accompanied with, or perhaps is due to the agency of, organisms which are the means of germinating or spreading disease. As might be expected albuminoid ammonia is usually found in calm weather in the atmosphere of cities.

Ammonia has been mentioned as an ultimate product of decay of nitrogenous organic nature; in the ordinary forms of decay and combustion, ammonia is the chief product, but it is usually attended in combustion with the formation, in small quantities, of nitrous and nitric acids, which may be considered as oxidation products. The extensive knowledge recently acquired, concerning the functions of organized germs, has shown that most forms of decay, and of purification as well, are dependent directly or indirectly upon their influence. Through the agency of the germ known as the niter ferment, for example, ammonia may be converted into nitric acid, and this change is constantly in progress where animal refuse accumulates, as in the vicinity of stables. The magnitude of these changes in nature will be appreciated when it is remembered that most of the niter of commerce has been formed in this manner, either naturally, as in the niter beds in hot countries, or artificially, as in the niter plantations of Sweden. Although nitric acid is the ultimate product of such changes, as an intermediary product, nitrous acid is formed in combustion, and both these acids may be detected in the atmosphere where it is receiving, in large quantities, the products of combustion.

In certain cities, including Cleveland, whose rapid development in wealth and population has been dependent, to a large extent, upon their proximity to immense deposits of cheap fuel, the sooty condition of the atmosphere has rapidly increased within recent years until it has attracted much attention with the feeling that such a condition is not conducive either to personal comfort or to health.

Since, so far as we are informed, a thorough examination of the atmosphere in these cities has not been made, it seemed to us of sufficient interest to undertake a study of the atmosphere of Cleveland with especial reference to the constituents which have been described above, with determinations, so far as practicable, of the quantities present.



As a means of ascertaining the quantity of soot deposited from the atmosphere, and also the amount of sulphuric acid removed from the atmosphere by snow, quantities of snow were collected for examination at the following localities which were assumed to represent an average condition of the city atmosphere,—McHenry St., Erie St., Covington St., and campus of the Case School of Applied Science; and the results, with certain data concerning the collection, are given in the following table:

Location.	Date.	Area.	Weight $H_2O$ from snow melted. Grams.	Weight soot. Gram.
(1) McHenry St.,	Feb. 19, 9 sq. by 1 in. dp.,		3583	0.3117
(2) Erie St.,	Feb. 16, Col. on roof,		3775	0.1709
(3) Covington St., Newburg,	Feb. 19,		3717	0.4143
(4) C. S. A. S.,	Mar. 22, 6½ sq. ft. by 1 in. dp.,		3850	0.1611
(5) " "	Mar. 27, 7½ sq. ft. by ½ in. dp.,		2000	.....

	Weight soot per liter.	Weight $H_2SO_4$ per liter.	Weight $NH_3$ per liter.
(1)	0.0875 gram	0.0152 gram	0.00007 gram
(2)	0.0452 "	0.0063 "	0.00001 "
(3)	0.1113 "	0.0212 "	0.00012 "
(4)	0.0418 "	0.0139 "	0.000003 "
(5)	.....	0.0070 "	.....

These numbers are interesting in showing the large quantity of soot that falls from the atmosphere with the larger amounts collecting at certain points than at others. The quantities of sulphuric acid are large at all points, but nearly three times greater at Covington St., Newburg, near large establishments, than in the more open area near the Case School of Applied Science. The determinations of ammonia indicate an excessive amount at Covington St., and the least at the Case School of Applied Science.

The specific gravity of the water obtained by melting the snow was also determined:

(1).....	1.0010
(2).....	1.0000
(3).....	1.0010
(4).....	1.0005
(5).....	1.0000

These specimens were collected after recent falls before the snow had been contaminated to any considerable extent. The quantity collected on the roof at Erie St. had fallen only a few hours previous to its collection.

On account of the absorptive property of soot it seemed probable that it should retain a considerable quantity of sulphuric acid after it had fallen from the air. For definite proof a quantity of soot was collected on the window sills in the attic of the chemical laboratory, where it had been blown in under the window from the outside. It had probably not been long in collecting. When moistened with water the soot gave a strong acid reaction on test paper, and analysis showed the presence of sulphuric acid.

1.3355 grams of the soot gave 0.00698 gram barium sulphate, equivalent to 1.91 per cent. sulphuric acid.

Another determination of sulphuric acid was made in soot collected in the chimney of a house.

0.4381 gram of this soot gave 0.0459 gram sulphuric acid, which corresponds to 3.17 per cent. sulphuric acid.

Sulphuric acid has invariably been found in testing soot collected in other places.

A noticeable characteristic of a sooty atmosphere and perhaps one of the most important, is the large quantity of soot deposited on the trunks and leaves of trees. In the absence of rain, soot must collect upon the leaves in sufficient quantity to interfere with their natural function of absorbing carbon dioxide. Since it appears that soot and dust absorb sulphuric acid, to a certain extent, from the atmosphere it seemed desirable to ascertain to what extent, if any, this acid collects on the bark of trees. At a point not far removed from manufacturing establishments quantities of bark were scraped from the trunk of a peach, a poplar, a cherry, a hickory, and an oak tree. Probably the kind of tree should not affect the deposition and absorption of acid except perhaps in the degree of roughness of the bark. Nevertheless there are decided differences in the amount of acid from the various sources. The following table gives the results of these determinations :

Variety of trees.	Area.	Total Wt. of bark.	Weight taken for analysis.	Wt. BaSO <sub>4</sub> .	Wt. H <sub>2</sub> SO <sub>4</sub> .	Wt. H <sub>2</sub> SO <sub>4</sub> per sq. foot.
Peach	245.3 sq. in.	17.5750	5.0008	0.0597	0.0251	0.0148
Poplar	280.0 "	3.7534	3.7534	0.0658	0.0277	0.0132
Cherry	200.0 "	2.8886	2.9896	0.0732	0.0308	0.0221
Hickory	400.0 "	3.1333	3.1333	0.0467	0.0196	0.0071
Oak	400.0 "	6.7886	5.0297	0.0352	0.0148	0.0053

In the order of the roughness of the bark the trees examined may be arranged as follows, with the peach as the least rough : peach, poplar, oak, hickory, cherry. Doubtless the deposition of soot containing acid upon the leaves is of even more serious consequence than upon the bark and the effects are clearly apparent on trees situated in the worst portions of a sooty atmosphere. The foliage of such trees exhibits an appearance of decay late in the summer months and the leaves fall early. We did not succeed in collecting specimens of leaves under suitable conditions to determine to what extent acid is retained on their surface.

Some attention has been given to the condition of the trees in such an atmosphere, but more especially with reference to the ravages of parasites that infest trees. In individual instances, no doubt, trees may be totally destroyed in this manner, but it is questionable whether the pernicious effects of a sooty atmosphere are not of more serious consequence on the trees as a whole. The corrosive action of an atmosphere impregnated with soot is daily manifest to the most ordinary observation. I have seen, in the country, nails withdrawn from a shingled roof seventy-five years after the shingles were laid, with the heads apparently unaffected, and the portion between the shingle and the board only slightly rusted away. In the atmosphere of a sooty city, as every one knows, after ten or fifteen years the nails on a roof are nearly consumed.

The effects of such an atmosphere on perishable property, such as certain forms of merchandise, are not so readily discernible, since this material is soon consumed by use. It is in libraries that the effects are most apparent. Fifteen years ago it was demonstrated by the late Professor W. R. Nichols that sulphuric acid is absorbed in bookbindings, and after some time the bindings begin to crumble; he found that the presence of the acid in deteriorated bindings may readily be shown.

The samples of air for examination, were collected at the following points, as fairly representing the different sections of the city.

(1) Campus of Case School of Applied Science, not far from the school buildings and those of Adelbert College. The line of the N. Y., St. Louis & Chicago R. R. is one-eighth of a mile distant toward the south-east.

(2) McHenry St.; closely inhabited, numerous manufactories 700-1,000 feet distant; a line of foundries, steel works, etc., extends three miles along the lake front, one-half a mile distant toward the north from this point. Most of the solid particles of soot fall to the ground within one-fourth to one-half a mile from the source.

(3) Rockwell St.; surrounded by large business blocks. The general condition of the atmosphere is bad on account of the soot, dust from the surrounding streets, and laxity in the enforcement of sanitary regulations.

(4) St. Clair St., near St. Lawrence; many large manufacturing establishments within 500 feet, on the lake shore, all using bituminous coal. When all are in operation, dense volumes of sooty smoke are sent forth into the atmosphere.

(5) West side; on the brow of the hill above the river near Pearl and Detroit Sts. Many locomotives pass below during the hour, and, on the river, tugs pass frequently. When the wind blows from the south-east, this locality is probably one of the worst in the city. The river itself doubtless aids the atmospheric pollution at this point since it is little better than an open sewer with a very sluggish current.

(6) South side, Jefferson St., a residence section with no factories near. In a north-easterly direction is a large ravine containing various kinds of decaying organic matter.

(7) Valley of the Cuyahoga, "Flats"; a very large number of factories of all kinds together with slaughter houses, rendering establishments, etc. Noxious vapors and disagreeable odors from the river invest this entire locality. In clear weather the smoke ascends for the particular benefit of the inhabited district on the neighboring bluffs. Circulation of the atmosphere is

slow in damp weather and the impure atmosphere remains in the valley.

(8) Genessee Avenue, near Superior St. ; a residence and farming district with no factories nearer than one-fourth of a mile.

(9) Mayfield, three miles outside of the city limits and six miles from the large manufacturing establishments of the city ; a farming section with no barns nearer than one-fourth of a mile of the point where the collection of air was made.

(10) Collinwood, three miles from the city limits, near the Lake Shore Railroad, where locomotives are constantly passing ; numerous barns close together, the nearest 900 feet distant.

Numerous determinations of carbon dioxide at different points in sections of country widely separated have shown no appreciable variation. On the average it is not far from four parts in 10,000 with a variation between three and five-tenths and four and five-tenths parts. Analyses of Cleveland air have shown some variation evidently depending upon the particular conditions at the point where the collection was made :

Locality.	Parts CO <sub>2</sub> per 10,000.
(1).....	3.52
(2)....	3.89
(3).....	4.01
(4).....	3.86
(5).....	4.52
(6).....	4.31
(7).....	4.77
(8).....	3.99
(9).....	3.68

We have attached no particular importance to the determination of carbon dioxide in connection with the principal object of this examination. The following numbers represent the quantity usually present in a city atmosphere :

	Parts in 10,000.
London, England.....	4.39
Glasgow, Scotland.....	5.02
Perth, " .....	4.12
Manchester, England.....	4.42
Cleveland .....	4.42

In determining soot in the atmosphere a measured volume of

air was drawn through a piece of combustion tubing partly filled with ignited asbestos and the carbon was determined by ignition, and absorption of the carbon dioxide as in ordinary combustions. The weights given in the following table are probably somewhat too low, since the soot is doubtless composed, for the most part, of hydrocarbons:

Locality.	Weather	Wind	Vol. of air at 0° and 76 cm. Liters.	Wt. CO <sub>2</sub> .	Weight soot in 1,000,000 cubic meters.
(1)	Clear	N.	94.0	0.0034 gram	9,875 grams
(2)	"	S. W.	70.2	0.0017 "	6,609 "
(3)	"	N. W.	88.2	0.0051 "	15,773 "
(5)	"	S. W.	92.5	0.0042 "	12,386 "
(5)	"	N. W.	88.7	0.0005 "	1,538 "
(6)	Cloudy	W.	89.3	0.0054 "	16,491 "
(6)	Clear	W.	91.3	0.0027 "	8,065 "
(8)	"	N. W.	94.3	0.0053 "	15,330 "
(8)	"	N. W.	77.9	0.0140 "	39,906 "

A clearer idea may be gained of the quantities of soot given above, if it is understood that 1,000,000 cubic meters is equivalent to the quantity of air contained within a space one mile square and a little more than one and one-fourth feet deep, and that the quantity of carbon, 39.664 grams calculated from analysis of the air collected at Genessee Ave., is equivalent to approximately 8.7 pounds. This very high result has no direct bearing on the quantity of soot in the atmosphere at this point, since it may be attributed to a high wind which filled the air with dust while the experiment was in progress. The air was collected at McHenry St., seven hours after rain had fallen. In certain conditions of the atmosphere frequently observed, there can be no doubt that the quantity of organic dust in suspension is very much larger than is represented by the values given above. The variable proportion of carbonaceous matter in the city air is shown in the duplicate samples collected at the West Side, the South Side, and Genessee Avenue. With the wind blowing from the north-west at the West Side the air is very clear, but in the direction of the south-east, as mentioned above, this section is in the direct line of the smoke from the river valley. Evidently these determinations serve to indicate merely the quantity in suspension in the air examined; but since the soot is rapidly

deposited, these values are, in no sense, a measure of the quantity escaping into the atmosphere.

In determining sulphur in the atmosphere in the form of sulphuric acid, a measured volume of air was drawn through a large U tube containing a solution of sodium hydroxide and broken glass, after passing through ignited asbestos. The alkaline solution was acidified with hydrochloric acid, oxidized with bromine, and the sulphuric acid precipitated with barium chloride. The quantities obtained are given in the following table:

Date.	Locality.	Weather.	Wind.	Velocity of air.
(1) Apr. 9, A. M.	C. S. A. S.	Clear	N. E.	53.9 liters
(2) " 9, P. M.	"	"	Variable	53.9 "
(3) " 13,	"	"	N. E.	6.25 miles 101.5 "
(4) " 19,	McHenry St.	Cloudy	S. W.	3.7 " 27.3 "
(5) June 13,	" "	"	W.	1.5 " 55.7 "
(6) Apr. 23,	Rockwell "	"	N. W.	29.4 "
(7) " 24,	St. Clair "	Hazy	N. W.	3.6 " 28.8 "
(8) " 27,	Riv. Val.	Clear	S. E.	5 " 27.6 "
(9) June 29,	" "	Cloudy	N.-S.	5.5 " 47.8 "
(10) Apr. 30,	W. Side	Clear	S. W.	1.5 " 28.3 "
(11) May 1,	S. Side	Cloudy	W.	4.5-18.3 " 28.0 "
(12) " 7,	Genessee Ave.	"	N. W.	8.7-2.5 " 28.6 "
(13) " 15,	Collinwood	Hazy	N. E.	44.2 "
(14) June 26,	Mayfield	Clear	S. W.	7.5 " 39.8 "

Locality.	Weight $\text{BaSO}_4$ .	Grams $\text{H}_2\text{SO}_4$ in 1,000,000 cu. met.
(1) .....	0.0030	23414
(2) .....	0.0028	21859
(3) .....	0.0053	20178
(4) .....	0.0027	42156
(5) .....	0.0022	16615
(6) .....	0.0033	47801
(7) .....	0.0011	16142
(8) .....	0.0033	50629
(9) .....	0.0033	29014
(10) .....	0.0057	56828
(11) .....	0.0042	63289
(12) .....	0.0023	33989
(13) .....	0.0000	.....
(14) .....	0.0007	7392

The variation in the quantity of sulphuric acid in the atmosphere is shown in the duplicate determinations at McHenry St., and the river valley, made at different dates. A negative result

at Collinwood is, perhaps, what might be expected in country air under certain conditions. And yet it seems that it was possible for sulphuric acid to be carried as far as Mayfield. It would be interesting to examine the atmosphere at different distances outside the city to ascertain how far the influence of the city air extends.

The following weights in grams of sulphuric acid in 1,000,000 cubic meters, have been found in the atmosphere of cities in England:

London .....	1669.935
Didsbury.....	1337.844
Blackpool.....	474.413
Buxton.....	1494.400
Manchester .....	2443.738

As already explained, sulphur sent forth into the atmosphere from the combustion of coal may escape complete oxidation and appear in part as hydrogen sulphide and in part as sulphurous acid. In testing for sulphurous acid in the atmosphere near the Case School of Applied Science, a measured volume of air was drawn through the alkaline solution for absorption, and in one portion the sulphuric acid was precipitated with barium chloride. The weight of barium sulphate corresponded to 20,276.36 grams of sulphuric acid in 1,000,000 cubic meters. To the remaining portion of the solution used for absorption bromine was added for oxidation, and the solution precipitated with barium chloride. The difference in weights corresponded to 33,033.1 grams of sulphuric acid in 1,000,000 cubic meters. In further confirmation of the presence of both sulphurous and sulphuric acids, another determination was made on the "Flats," near the Central viaduct, on an exceptionally clear day. In eighty-six liters of air aspirated, the total weight of barium sulphate, after oxidation, corresponded to 0.0058 gram barium sulphate, and the weight of barium sulphate before oxidation was equivalent to 0.0028 gram barium sulphate, the difference, 0.0031, representing the sulphurous acid in the total volume of air aspirated. The quantity of sulphuric acid present was, therefore, represented by 11,851 grams, and the sulphurous acid by 12,512.6 grams in 1,000,000 cubic meters.

In the atmosphere of other cities, notably in Manchester,



England, and Lille, France, sulphurous acid has been determined, and it is probable that it may always be detected in the atmosphere where it receives large quantities of smoke from the combustion of coal.

The presence of ammonia as a normal constituent of the atmosphere has already been mentioned, and under ordinary conditions it does not collect in sufficient quantity to be injurious. Nevertheless, it seemed of interest to ascertain to what extent this constituent collects in an atmosphere contaminated with soot. In collecting ammonia, a definite volume of air was drawn through a dilute solution of hydrochloric acid, and both free and albuminoid ammonia were determined by the methods ordinarily employed in water analysis. After the free ammonia was distilled the residual solution was oxidized with alkaline permanganate until there was no further evolution of ammonia, and both sets of distillates nesslerized. The following tables give the quantity of free and albuminoid ammonia from the quantity of air aspirated in each locality and the state of the weather.

	Date.	Locality.	Weather.	Wind Direc.	Wind Veloc.	Volume of air in liters.
(1)	Apr. 6,	C. S. A. S.	Clear	N. W.	9 m.	48.024
(2)	" 6,	"	Cloudy	"	6 "	46.071
(3)	" 19,	McHenry St.	"	S. W.	4 "	20.391
(4)	June 13,	" "	"	W.	1.5 "	6.941
(5)	Apr. 23,	Rockwell "	"	N. W.	4 "	22.334
(6)	" 24,	St. Clair "	Hazy	N. W.-W.	2 "	22.163
(7)	June 20,	" " "	Clear	N.	"	6.963
(8)	Apr. 30,	West Side	"	S. W.	18 "	21.282
(9)	" 27,	" "	"	N. W.	1 "	7.054
(10)	May 1,	South Side	Cloudy	W.	1 "	20.971
(11)	June 22,	" "	Clear	W.	0.5 "	7.092
(12)	May 7,	Genessee Ave.	Cloudy	N. W.-S. W.	8.7-25m	6.622
(13)	June 21,	" "	Clear	N. W.	1 m.	6.829
(14)	" 26,	Mayfield	"	S.	7.5 "	6.781
(15)	" 29,	River Valley	"	N. W.	6.5 "	6.862

	Total free NH <sub>3</sub> .	Total Albuminoid NH <sub>3</sub> .	Free NH <sub>3</sub> in 1,000,000 cu. met.	Albuminoid NH <sub>3</sub> in 1,000,000 cu. met.
(1)	0.00000051	0.0000071	106.10 grams	147.84 grams
(2)	0.00000490	0.0000045	106.35 "	97.67 "
(3)	0.00002180	0.0000113	1070.20 "	557.50 "
(4)	0.00000210	0.0000021	302.50 "	298.90 "
(5)	0.00000780	0.0000035	357.20 "	158.90 "
(6)	0.00002330	0.0000051	1051.10 "	230.10 "

	Total free $\text{NH}_3$ .	Total Albuminoid $\text{NH}_3$ .	Free $\text{NH}_3$ in 1,000,000 cu. met.	Albuminoid $\text{NH}_3$ in 1,000,000 cu. met.
(7)	0.0000014	0.0000023	198.7	329.1 grams.
(8)	0.0000082	0.0000037	385.5	173.8 "
(9)	0.0000059	0.0000030	836.9	430.9 "
(10)	0.0000169	0.0000043	806.4	202.5 "
(11)	0.0000015	0.0000007	214.5	100.6 "
(12)	0.0000086	0.0000031	1373.0	489.5 "
(13)	0.0000030	0.0000034	440.6	492.0 "
(14)	0.0000035	0.0000019	510.2	282.8 "
(15)	0.0000054	0.0000010	787.7	150.1 "

We have found on record but few determinations of free and albuminoid ammonia, but similar determinations have been made in certain cities abroad, the results of which afford an interesting comparison with those we have obtained.

	Grams free $\text{NH}_3$ in 1,000,000 cu. met.	Grams albuminoid $\text{NH}_3$ in 1,000,000 cu. met.
London.....	61.286	150.919
Glasgow.....	78.196	304.974
Innellan.....	52.281	137.832

These numbers represent much smaller quantities of albuminoid ammonia, and still smaller quantities of free ammonia than appear in the results of our determinations.

It has long been known that nitrous acid and nitric acid are contained in the products of combustion from fuels containing nitrogen as most fuels do. These acids represent a more advanced stage of oxidation than ammonia; they are derived to a certain extent, it may be, from the oxidation of atmospheric nitrogen; and they may also be detected in the products of respiration. Ammonium nitrate may be found in dew and it seems to be present in larger quantities in spring than in summer and more at night than during the day. These acids are, therefore, normal constituents of the atmosphere under natural conditions, and the minute quantities usually present can not be considered harmful.

In testing for nitric acid we used as an indicator phenolsulphonic acid prepared by dissolving phenol in concentrated sulphuric acid and for comparison, a solution of potassium nitrate in which one cc. contained 0.000001 gram nitrogen. For nitrous acid, sulphanilic acid and naphthylamine hydrochloride were used as indicators with a solution of sodium nitrite, in which one cc. contained 0.000001 gram nitrogen as a means of com-

parison. A measured volume of air was drawn through a solution of sodium hydroxide prepared from metallic sodium, and definite quantities of this solution were used in each determination.

The following tables give the quantities of nitrous and nitric acids found in experiments conducted at different localities with other data of the collection :

## NITROUS ACID.

Date.	Place.	Weather, &c.	Grams HNO <sub>2</sub> in 1,000,000 cub. met.
Apr. 17,	C. S. A. S.	Clear W. N. E.....	6.767
May 11,	"	" W. N. W.....	0.000
July 2,	"	Cloudy Calm.....	6.955
April 19,	McHenry St.	" W. S. W.....	119.277
June 30,	" "	Clear W. N. W.....	73.976
April 23,	Rockwell "	Cloudy Damp.....	152.785
June 16,	" "	Clear W. N. W.....	8.856
Apr. 24,	St. Clair "	" W. N. W.....	126.614
June 20,	" "	" W. N.....	135.500
June 29,	River Valley	Cloudy W. N. W.....	0.607
May 4,	West Side	Clear W. N. W.....	15.206
June 27,	"	" W. N. W.....	19.945
June 22,	South Side	" W. W.....	1.239
May 7,	Genessee Ave.	" W. N. W.....	5.833
June 21,	" "	" W. N. W.....	7.228
May 15,	Collinwood	Cloudy Calm....	4.564

## NITRIC ACID.

Date.	Place.	Grams HNO <sub>3</sub> per 1,000,000 cub. met.
April 17,	C. S. A. S.....	674.5
May 11,	" .....	560.0
April 19,	McHenry St.....	703.8
June 13,	" " .....	54.99
April 24,	St. Clair St.....	520.5
June 20,	" " .....	144.0
April 27,	River Valley.....	704.0
June 27,	" " .....	68.8
April 30,	West Side .....	1063.6
May 4,	" " .....	367.6
June 27,	" " .....	66.9
May 1,	South Side.....	61.8
June 22,	" " .....	153.8
May 7,	Genessee Avenue .....	333.6
June 21,	" " .....	129.4
May 15,	Collinwood .....	424.0
June 16,	Rockwell St.....	544.8
June 26,	Mayfield .....	44.5

The variation in the proportion of both nitrous and nitric acids under different conditions is very marked, as shown in the samples of air collected in the river valley, the West Side, and McHenry St.

From the results of this examination it is evident that a city atmosphere, contaminated by the universal consumption of bituminous coal, where no efforts are made to prevent the escape of soot, soon reaches a stage in which it is destructive to property and not conducive to health. In this respect the atmosphere of Cleveland is, doubtless, no worse than that of other cities, and, perhaps, in a better condition than some that use the same fuel. Under the usual conditions of life in cities, sanitary regulations require careful attention and constant supervision.

### A NEW FORM OF WATER-OVEN AND STILL.<sup>1</sup>

BY LEWIS WILLIAM HOFFMANN AND ROBERT W. HOCHSTETTER.

Received November 2, 1894.

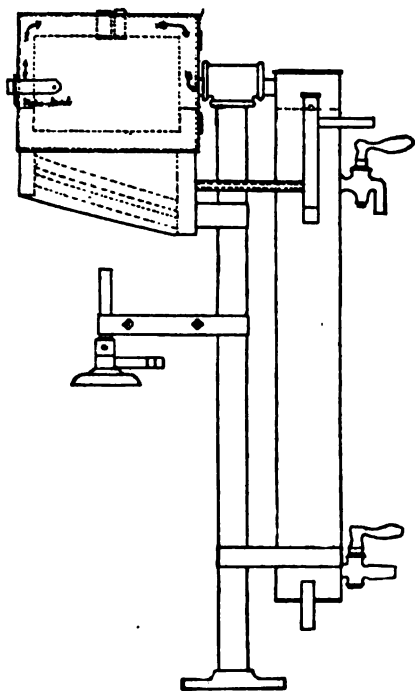
In the use of the ordinary form of water-oven we have been impressed with the fact that there are several disadvantages connected with that form of this apparatus. For instance, there is the necessity for refilling it from time to time, with the consequent fall in temperature and loss of time; there is the waste of steam which might be condensed to the always-useful distilled water, and we have had trouble in obtaining a constant temperature of 100° C. To obviate these difficulties we have devised the combined oven and still which we describe here—a piece of apparatus that has an automatic feed, a worm for condensing the steam and an arrangement of the heating surface so as to provide for perfect circulation and quiet boiling, with steady and abundant generation of steam.

The combination of still and oven is not new, for in the April, 1892, number of the *Journal of Analytical and Applied Chemistry*, Herbert M. Hill describes such a piece of apparatus in use in the Buffalo University laboratory. Except for the combination it bears little resemblance to our apparatus.

In our form of apparatus, the heating surface consists largely of a series of pipes, connected with water boxes at each end.

<sup>1</sup> Read before the Cincinnati Section, October 15, 1894.

These pipes, through which the water circulates, are inclined so as to afford an easy ascent for the steam generated in them, as



the result of the heat applied to their outer surface. The source of heat is an ordinary Bunsen burner, used with a wing-tip, so as to spread the flame over the surface of the pipes. The pipes are of small diameter so as to afford a large heating surface in proportion to the amount of water passing through them.

The steam is carried off at a point about half-way up the side of the oven and passed through a block-tin condenser. To reach the condenser the steam must pass over the top of the drying-chamber, as the water-level in the oven is kept about one-fourth of the distance

between the top and bottom, thus acting as a lute and compelling the steam to pass up and over in order to escape. The water used in cooling the worm also serves as feed-water for the oven, and as it passes from the bottom to the top of the condenser, absorbs so much heat as to enter the water-box already heated almost to the boiling-point. The feed-pipe is so small that the circulation between condenser and oven is slow but constant. A stop-cock is provided at the top of the condenser, for drawing off hot water if desired. A small hole in the door and another in the top provide for ventilation of the drying chamber. Sedimentation takes place in the condenser so that almost clear water goes into the heating-pipes.

To the factory chemist, having always a plentiful supply of condensed steam at his disposal, this piece of apparatus may not seem of much value, but to the analyst, a combination of

still and water-oven means a saving of time, trouble, and, in some cases, expense.

The advantage derived from the arrangement of pipes for receiving heat, (an idea borrowed from the Babcock-Wilcox boiler,) may be conceived from the statement that while in the oven which we have, the heating surface measures 82.8 square inches, but seven square inches of this area is the bottom of the oven, the rest being made up by the pipes and the sides of the water-boxes at each end.

Now as to the work done by the apparatus. The oven which we have in our laboratory will get up steam in four minutes after the flame is lighted, and at the expiration of six and two-tenths minutes will be delivering distilled water. This is with a Bunsen burner consuming three cubic feet of gas per hour. With a burner consuming twice as much gas, one and three-tenths minutes is gained in steaming, and two and two-tenths minutes in delivering water.

The still delivers water at the rate of two and one-fourth quarts per hour or thirteen and one-half gallons in twenty-four hours—this with a three-foot gas-burner. A patent automatic still which we have hitherto been using, consumes six cubic feet of gas per hour, and delivers two quarts of water an hour, or twelve gallons in twenty-four hours, although the claim made for it by the makers is fifteen gallons in twenty-four hours.

The temperature in the drying chamber of our form of apparatus ranges from  $98^{\circ}$  to  $101^{\circ}$  C., so that it may be said to average  $100^{\circ}$ .

The advantages claimed for our form of apparatus are as follows:

A constant temperature of  $100^{\circ}$ , which in our experience, can not be obtained with the ordinary form of oven.

A large yield of distilled water, with a small expenditure of heating material, and practically no cost, as the water-oven is nearly always in use in a working laboratory.

Hot water always at command.

Small space occupied by both oven and still.

General convenience of arrangement.

MT. AUBURN, CINCINNATI,  
November, 1894.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE  
UNIVERSITY OF MICHIGAN.]

## THE DETERMINATION OF NICKEL IN NICKEL-STEEL.

E. D. CAMPBELL AND W. H. ANDREWS.

Received December 24, 1894.

SINCE publishing his former method for the determination of nickel in nickel-steel (This JOURNAL, 16, 96), the author has been endeavoring to perfect another method which should be an improvement over the first one. Such accurate results have been obtained in so short a time by this method that it is thought desirable to give the details of manipulation.

Place a one gram sample of nickel-steel in an Erlenmeyer flask of about one-half liter capacity. Add twenty-five cc. of nitric acid (1.20) and boil until dissolved and nitric oxide is boiled out of the flask. Meanwhile, dissolve thirteen grams of sodium pyrophosphate in seventy-five cc. of warm water. This solution must not be boiled as the pyrophosphate is thereby converted to the orthophosphate.

After complete solution, filter the sodium pyrophosphate and add it to the cooled solution of the steel. This will give a heavy, white precipitate of ferric pyrophosphate. Add, a little at a time, with constant agitation, a clear twenty per cent. solution of sodium carbonate until the precipitate of ferric pyrophosphate just dissolves and the solution attains a dull, olive-green color.

An excess of sodium carbonate must be carefully avoided, as the subsequent precipitation of nickel will not be complete if this is not done. With an excess of the carbonate the solution turns red, so that color may be used as a guide to the required amount. For a one gram sample, fifty to fifty-five cc. of twenty per cent. sodium carbonate is usually sufficient.

After redissolving with sodium carbonate, filter through asbestos, receiving the solution in a one-half liter Erlenmeyer flask; wash the filter with water sufficient to rinse out the original flask and to insure complete transference of the solution. Now add to the solution two grams of potassium xanthate freshly dissolved in twenty to twenty-five cc. of water. Stopper the flask and shake at frequent intervals for ten minutes. The nickel will be

completely precipitated as xanthate, together with any copper the steel may contain, but perfectly free from manganese and almost free from iron. Filter as rapidly as possible through asbestos, using a pump, and wash the brick-red nickelous xanthate four or five times with freshly prepared one per cent. potassium xanthate.

The solution of potassium xanthate used for precipitating, as well as that used for washing, should be prepared by adding to the desired amount of salt sufficient water for solution, but should not be allowed to stand longer than fifteen or twenty minutes before using as it slowly decomposes. The dry salt is stable.

Dissolve the washed precipitate off the filter by allowing twenty cc. of freshly diluted fuming nitric acid to fall little at a time on it. The dilute fuming nitric acid should be prepared just before using by pouring ten cc. of water into ten cc. of fuming nitric acid. Catch the solution of the xanthate precipitate in a small Erlenmeyer flask. Wash the filter two or three times with hot water, then pass through five cc. of dilute sulphuric acid (2:3) and wash this out with more hot water. Boil the solution in the flask rapidly until the nitric acid is completely expelled and sulphuric anhydride fumes begin to rise. Cool, add twenty to twenty-five cc. of water, heat nearly to boiling, and, when all is in solution, pass in hydrogen sulphide for two or three minutes. Allow to stand until the cupric sulphide has settled. Filter and wash with hot water containing a little hydrogen sulphide.

Boil the filtrate, containing the nickel and a very small amount of iron, until hydrogen sulphide is expelled, add a few drops of hydrogen peroxide, or a few milligrams of sodium peroxide to oxidize the iron, and boil, then precipitate the iron with a very slight excess of ammonium hydroxide. Boil, filter, and wash once or twice with hot water. Dissolve the small precipitate of ferric hydroxide off the filter with five cc. of dilute sulphuric acid (2:3) and reprecipitate with a slight excess of ammonium hydroxide. Boil and filter into the original filtrate. This solution will contain all the nickel free from iron, manganese, and copper. The nickel may be determined in either of the following ways:



1. *Electrolytically*.—Place the united filtrates from the ferric hydroxide in a platinum dish having a capacity of about 200 cc., add thirty cc. of a ten per cent. solution of disodium hydrogen phosphate, then twenty-five cc. of strong ammonium hydroxide. The solution should have a bulk of about 175 cc. Electrolyze for twelve hours with a current of 0.14 amperes per 100 sq. cm. area of the dish, having the electrodes about one-half cm. apart.

The precipitate of nickel obtained in this way is perfectly clear and bright, hardly to be distinguished from the platinum on which it is deposited.

Wash the precipitated nickel with warm water then with alcohol. Dry and weigh as usual. For accurate work it is more satisfactory to use a second platinum dish washed and dried like the first, as a counterpoise.

2. *Volumetrically*.—Place the united filtrates from the ferric hydroxide in a medium sized Erlenmeyer flask and cool until cold. The solution should have just enough free ammonia to give a slight but distinct odor; if this is not present at this stage, add a few drops of ammonium hydroxide. Add five cc. silver nitrate indicator (made by dissolving five-tenths gram silver nitrate in 1,000 cc. of water). Add five cc. of a two per cent. solution of potassium iodide, which give the solution an opalescence due to the presence of silver iodide in suspension.

Run in standard potassium cyanide (one cc. = 0.001 gram nickel) until the solution becomes clear and bright. The titration depends upon the fact that so long as there is any nickel uncombined with potassium cyanide in the form of the double cyanide, the silver iodide will remain undissolved, but as soon as the nickel has all been changed the silver iodide dissolves forming potassium silver cyanide and the solution becomes perfectly clear.

Subtracting a correction necessary for the titration of the indicator from the total amount of potassium cyanide used, gives the amount necessary for the nickel.

*Standard Solutions Required*.—Standard nickel solution: This can be most easily prepared from pure nickel wire. The commercially pure nickel wire usually contains 98.5–99.5 per cent.

nickel. If this wire is used for making the standard solution, take such a weight as will represent one gram of pure nickel, dissolve in a No. 3 beaker with twenty-five cc. nitric acid (1.42) and evaporate just to dryness on the water-bath. Moisten with a few drops of nitric acid, add about twenty-five cc. of water, and heat to solution. When the nickel is dissolved, dilute to fifty or sixty cc., add six grams of sodium acetate dissolved in a little water, heat nearly to boiling until the ferric basic acetate separates. Filter, and wash thoroughly with hot water. Add five cc. of sulphuric acid to the solution, transfer to a graduated liter flask, cool, and dilute to 1,000 cc.

*Standard Potassium Cyanide.*—Dissolve four and five-tenths grams of potassium cyanide in water and dilute to 1,000 cc. This must be standardized against the standard nickel solution.

Run in from a burette twenty-five to thirty cc. of the nickel solution into a medium sized Erlenmeyer flask, dilute with water to about 100 cc., add ten cc. of dilute sulphuric acid (2:3); then add ammonium hydroxide carefully until a slight but distinct odor of ammonia is perceptible. Add five cc. of silver nitrate indicator, five cc. of two per cent. potassium iodide and titrate with potassium cyanide until the solution brightens. Correction for the indicator is found by proceeding exactly as above, except that the standard nickel solution is omitted.

The potassium cyanide is quite stable, weakening, however, gradually on standing. The deterioration amounted from five-hundredths to one-tenth cc. in twenty-five cc. during one week.

In order to test fairly the accuracy of the recovery, the varying amounts of pure nickel wire were weighed and dissolved by my private assistant, who turned them over to Mr. Andrews as strictly unknown samples. Weighed amounts of iron wire were then added and the solution proceeded with as if it were an ordinary sample of steel.

Two hours is sufficient time to get the solution ready for electrolysis or for titration.

The following table will show the accuracy of the results obtained, where the amount of nickel present was strictly unknown to the operator until the analysis was completed :

Iron added. Grams.	Nickel taken. Gram.	Nickel recovered. Gram.	Gain and loss.		Method.
			+	-	
0.2105	0.08892	0.08910	+ 0.00018		Electrolytically.
1.0000	0.03430	0.03435	+ 0.00005		"
1.0041	0.05298	0.05345	+ 0.00047		"
1.0043	0.10824	0.10825	+ 0.00001		"
2.0043	0.02690	0.02740	+ 0.00050		"
1.0010	0.00100	0.00089	- 0.00011		Volumetrically.
1.0086	0.06578	0.06532	- 0.00046		"
1.0066	0.07582	0.07583	+ 0.00001		"
1.0057	0.08017	0.08050	+ 0.00033		"
1.0071	0.09389	0.09381	- 0.00008		"

ANN ARBOR, MICHIGAN,  
December 18, 1894.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE  
POLYTECHNIC INSTITUTE. VI.]

## THE VOLUMETRIC DETERMINATION OF PHOSPHORUS IN STEEL AND CAST IRON.<sup>1</sup>

BY W. A. NOYES AND J. S. ROYSE.

Received January 3, 1895.

IN a previous paper<sup>2</sup> one of us, with Mr. E. D. Frohman, showed that in the reduction of molybdic solutions by means of Jones' reductor, the molybdenum is reduced to a form corresponding to the oxide  $\text{Mo}_2\text{O}_3$ . We also showed that the reduced solution is very easily oxidized by exposure to the air, and we were led to believe this would account for the difference between the theoretical factor for the calculation of the phosphorus equivalent of a permanganate solution from its iron equivalent, and the empirical factor as given by Dudley and Pease.<sup>3</sup>

In a private communication, however, Dr. Dudley has very kindly called our attention to the fact that he obtained the same results when following the directions for reduction given in our paper as when following the method which he had previously used. As the difference between his results and ours corresponded to only three-tenths or four-tenths cc. of the permanganate solution used, and the results obtained by Mr. Frohman

<sup>1</sup> Read at the Boston Meeting, December 28, 1894.

<sup>2</sup> This JOURNAL, 16, 553.

<sup>3</sup> This JOURNAL, 16, 230.

were not sufficiently accordant to establish the point in question, it became necessary to repeat that part of the work. Accordingly, the following series of determinations was made, following, as closely as possible, the directions given by Dudley and Pease.<sup>1</sup> The results are given in per cents., on the basis of one gram of steel.<sup>2</sup>

Steel No.	Phosphorus present.	Phosphorus found.	
		By theoretical factor.	By factor of Dudley and Pease.
Steel No. 1.....	0.040	0.040	0.045
" " 1.....	0.040	0.0354	0.0397
" " 2.....	0.053	0.0525	0.059
" " 2.....	0.053	0.0525	0.059
" " 3.....	0.032	0.0264	0.0296
5 grams cryst. $\text{FeSO}_4$ + 0.0011 gram cryst. $\text{Na}_2\text{HPO}_4$ .....	0.010	0.0035	0.0039
5 grams cryst. $\text{FeSO}_4$ + 0.0130 gram cryst. $\text{Na}_2\text{HPO}_4$ .....	0.113	0.127	.....
5 grams cryst. $\text{FeSO}_4$ + 0.0097 gram cryst. $\text{Na}_2\text{HPO}_4$ .....	0.084	0.091	.....
5 grams cryst. $\text{FeSO}_4$ + 0.0109 gram cryst. $\text{Na}_2\text{HPO}_4$ .....	0.094	0.106	.....
1 gram steel No. 3 + 0.0068 gram cryst. $\text{Na}_2\text{HPO}_4$ .....	0.091	0.097	.....
1 gram steel No. 3 + 0.0026 gram cryst. $\text{Na}_2\text{HPO}_4$ .....	0.055	0.054	0.0061

The first result is evidently wrong for some unknown reason. Omitting this, the results with steels Nos. 1 and 3 show conclusively that the factor of Dudley and Pease is correct for those steels and the statement of our first paper was erroneous. As regards steel No. 2 the case is different. Dudley and Pease explain the higher results obtained with this steel as due to arsenic which it contains. The results of the last determination in the table, and, still more, the results obtained by another method and given below, lead us to believe that this is not the case, but that for a steel containing 0.055 of phosphorus the theoretical factor gives very nearly correct results.

From the examination of the table as a whole it becomes apparent, at once, that, while the factor given by Dudley and Pease gives results nearly or quite correct for steels containing 0.03 to

<sup>1</sup> *J. Anal. Appl. Chem.*, 7, 108. This JOURNAL, 15, 519.

<sup>2</sup> This set of determinations was made by W. A. Noyes.

0.04 per cent. of phosphorus, it fails entirely so soon as the amount present is either above or below these limits. The reason is, we believe, apparent. When the amount of phosphorus is less than 0.05 per cent., a part of it escapes precipitation, and hence, a larger factor than the theoretical is required. When the amount of phosphorus is as great as 0.08 per cent. or more, however, the yellow precipitate probably carries down with it at 55° C., some free molybdic anhydride, and even the theoretical factor gives too high results. If we retain the method in its present form, therefore, it will be necessary to use several different empirical factors, or to apply a correction varying with the amount of phosphorus present in the steel under examination. We believe such a course is open to very serious objection and that it should be avoided, if possible. The use of a variable correction implies that the yellow precipitate is not a pure chemical compound, but that it has a variable composition dependent on the amount of phosphorus present. If we admit this, it is evident that the method is not a suitable one on which to base an accurate determination, for a compound or mixture of variable composition is liable to be seriously affected by even slight changes in manipulation, changes which are sure to occur in different hands and different laboratories.

These considerations led us to endeavor to modify the method in such a manner as to secure, if possible, a practically complete precipitation of very small amounts of phosphorous and also to secure the precipitation in the form of a compound of definite composition and independent of the amount of phosphorus present. The considerations which have guided us in the study are as follows: first, the precipitation would be more rapid in a more concentrated solution; second, the precipitation must be at a lower temperature than 55° to prevent the contamination of the precipitate with molybdic anhydride; third, the precipitate is formed more rapidly in a more nearly neutral solution; and fourth, the presence of ammonium nitrate hastens the formation of the precipitate, probably because ammonium enters into its composition.

Without going into the details of unsuccessful experiments, we will give the method which we have found most satisfactory.

We give details for reagents and apparatus, though most of these details are a repetition of those given by Dudley and Pease.

#### REAGENTS AND APPARATUS.

*Nitric Acid.*—One part of concentrated acid (1.42) to two parts of water by volume. This gives an acid of sp. gr. 1.18.

*Oxidizing Permanganate Solution.*—Twelve and one-half grams of potassium permanganate in one liter of water.

*Ferrous Sulphate.*—The crystallized non-effloresced salt, *free from phosphorus*.

*Ammonia.*—Concentrated, sp. gr. 0.90; and dilute, sp. gr. 0.96.

*Molybdic Solution.*—Dissolve 100 grams of molybdic anhydride in 400 cc. of ammonia (0.96), filter and pour the solution slowly, with constant stirring, into 1,000 cc. of nitric acid (1.20). Warm to 45°, add one cc. of a ten per cent. solution of crystallized sodium phosphate, stir vigorously, and allow to stand in a warm place over night before using. The addition of the sodium phosphate was suggested by Dr. Dudley and has the two-fold object of precipitating anything liable to contaminate the yellow precipitate and of leaving the solution saturated with the compound which is to be precipitated by it. Our experience leads us to think that the solution keeps better in the dark. It is always safer to filter it immediately before it is used and the solution must, of course, be absolutely clear. If pure, it will be almost or quite colorless, but we have found that a somewhat yellow solution prepared as above, gave us results nearly or quite identical with those obtained with a colorless solution.

*Acid Ammonium Sulphate.*—To one half liter of water add twenty-seven and one-half cc. of ammonia (0.96) and twenty-four cc. of concentrated sulphuric acid and make up to one liter.

*Potassium Permanganate for Titration.*—Dissolve four grams of potassium permanganate in two liters of water, heat nearly to boiling for an hour, allow to settle over night, and filter with the pump, using an asbestos filter prepared after the manner of Gooch on a small perforated porcelain plate placed in the bottom of a large funnel. Use very great care that the solution does not come in contact with india-rubber or any kind of organic matter and keep in a clean glass-stoppered bottle, free from

manganese oxides. We find that a solution prepared in this manner keeps perfectly and is not affected by the light.

We prefer to standardize with freshly crystallized and thoroughly air-dried ammonium oxalate dissolved in water with the addition of a little dilute sulphuric acid (instead of considerable concentrated acid as advised by Fresenius) and with ferrous ammonium sulphate freshly crystallized in small crystals from a slightly acid solution, the crystals being thoroughly washed and quickly air-dried in a thin layer, using the factors  $\frac{1}{112}$  and  $\frac{1}{7}$  respectively to calculate the iron equivalent<sup>1</sup>. The phosphorus equivalent is obtained by multiplying the iron equivalent by  $\frac{31}{56 \times 56} = 0.01538$ .

*Jones' Reductor.*—A piece of moderately heavy glass tubing thirty-five cm. long and having an internal diameter of about two cm., is drawn out at one end to pass through the stopper of a filtering flask. In the bottom of the tube is placed a small perforated porcelain plate and on this is prepared an asbestos filter, practically a Gooch filter. This filter should offer enough resistance so that a reduction will occupy two or three minutes. The tube is nearly filled with powdered zinc, which is then washed with dilute sulphuric acid (1:20 by volume). Blank determinations are made as follows: To 180 cc. of water, add twelve cc. of ammonia (0.96) and ten cc. concentrated sulphuric acid. Pass the solution through the reductor and follow with 200 cc. of water, *taking care that no air passes through the reductor*. It is easily shown, qualitatively, that hydrogen peroxide is formed by passing air and water alternately through the reductor. After standing, even for a few minutes, the reductor should be rinsed with dilute sulphuric acid before use. Blank determinations should be made frequently and the amount of

<sup>1</sup> The method given by Dudley and Pease (This JOURNAL, 15, 321.) has given me practically identical results with the above methods, also piano wire, considering it as pure iron, the impurities in iron, some of them, requiring more permanganate than iron itself. The following results were obtained:

Iron wire (Fresenius' method).....	0.003199
Ammonium oxalate.....	0.003209
Ferrous ammonium sulphate.....	0.003209
Dudley's steel.....	0.003179
" " .....	0.003205
" " .....	0.003208

W. A. NOYES.

permanganate required should be subtracted from that found in an analysis. The blanks should not take more than two-tenths to three-tenths cc. of permanganate. Ours are usually less than two-tenths cc. We do not think it advisable to use the same reductor for both iron and molybdenum solutions.

#### ANALYTICAL PROCESS.

Weigh two grams of steel<sup>1</sup> to an accuracy of two mgms., put it in a 500 cc. (16 oz.) flask, add fifty cc. of nitric acid (1.18), and warm, only gently, till solution is complete, (our experience leads us to think some phosphorus may escape if the gases in the flask become colorless before solution is complete); then boil for one minute, add ten cc. of the permanganate solution (one and one-fourth per cent.), boil till the pink color disappears, add ferrous sulphate carefully, with shaking, till the solution clears, cool to about 50°, add eight cc. ammonia (0.90), insert the stopper, and shake till any precipitate which forms redissolves; cool or warm till the solution is as many degrees above or below 60° as the molybdic solution is below or above 27°, add sixty cc. of molybdic solution, insert the rubber stopper, and shake by hand or with a machine for five minutes; allow to settle for five minutes, filter through a nine cm. filter of rather fine texture, wash with the acid ammonium sulphate solution, putting five or ten cc. at a time into the precipitation flask and pouring from that all around the upper edge of the filter. The filtrate and washings must be absolutely clear. Wash till five cc. of the washings give no brown color with a few drops of dilute hydrogen sulphide water. Pour over the precipitate twelve cc. of ammonia (0.96) diluted to twenty-five cc., allow the solution to run into the precipitation flask, wash with 100 cc. of water, add eighty cc. more of water and ten cc. of concentrated sulphuric acid, pass the solution through the reductor and follow it with 200 cc. of water, *taking care that no air passes through the reductor* during reduction or washing. Titrate the solution, *at once, in the reductor flask*.

With steels high in phosphorus, the ammoniacal solution of the yellow precipitate may be made up to a known volume and an aliquot part taken for reduction.

<sup>1</sup> Dr. Dudley suggested the use of two grams of steel.



For cast iron low in phosphorus, the method may be carried out exactly as given for steel. The method may also be used without modification other than the use of a larger amount of ammonia for solution of the yellow precipitate and the use of an aliquot part of the solution for reduction, for cast iron high in phosphorus. We prefer, however, in that case, to use one gram of the iron, dissolve, oxidize, clear, and neutralize as usual, using twelve cc. of ammonia. Then the solution is made up to 150 or 250 cc. and ten cc., or more, taken, enough water added to make fifty cc., the solution warmed to 60° and sixty cc. of molybdic solution added. The remainder of the process is as above for steel. The residues insoluble in nitric acid may require examination as usual.

The process as here described has given us the results stated in the table below. No determinations which have been made by this method have been omitted. Steels Nos. 1, 2, and 3 were kindly furnished us by Dr. Dudley, and are the same as those described in this JOURNAL, 16, 217, and the gravimetric determinations given are the very careful ones reported in that paper. Steel "a" was also furnished us by Dr. Dudley with the statement that it contains, by their determination, 0.016 per cent. phosphorus, and is the lowest they have. Steel C is a tool steel containing, probably, about one per cent. of carbon, and, by our own gravimetric determination by the combined acetate-molybdate-magnesia method<sup>1</sup>, using ten grams of the steel, 0.021 per cent. of phosphorus. Steel A is a mild steel containing about 0.17 per cent. carbon and, by the molybdate-magnesia method, using five grams, 0.129 per cent. phosphorus. We do not place as much reliance on this gravimetric determination as on the other.

The gravimetric determinations for the cast iron were made as follows: one gram of the iron was dissolved in fifty cc. of nitric acid (1.18) and treated exactly as in our directions for steel. The ammoniacal solution of the yellow precipitate was made up to 150 cc. and two portions of ten cc. each were taken for reduction. These portions gave determinations 18-21 of the table. The remainder of the ammoniacal solution was concentrated in a platinum dish and then precipitated with magnesia mixture.

<sup>1</sup> This JOURNAL, 16, 221.

The magnesium pyrophosphate, after weighing, was dissolved in hydrochloric acid and evaporated to separate silica. In the first determination no silica was found; in the second there was an appreciable amount. The gravimetric determinations gave 1.75 and 1.79 per cent. of phosphorus, respectively.

In order to determine if more phosphorus could be obtained by solution in aqua regia, one gram of the iron was dissolved in thirty cc. of a mixture of equal volumes of concentrated nitric and hydrochloric acids; the solution was made up to 150 cc.; ten cc. were placed in a porcelain dish with five cc. of concentrated nitric acid, evaporated to dryness, and heated to 200° for one-half hour, the residue taken up with fifty cc. of nitric acid (1.18), nineteen cc. of ammonia added, and the solution precipitated as usual. This method gave the determinations 22 and 23 of the table. Determinations 24 and 25 of the table were made by the method recommended above for cast iron.

	Gravimetric determination.	Volumetric determination.
1. Steel No. 1.....	0.040 per ct.	0.037 per ct.
2. " " 1.....	0.040 "	0.040 "
3. " " 1.....	0.040 "	0.041 "
4. " " 1 <sup>1</sup> .....	0.040 "	0.0404 "
5. " " 2.....	0.053 "	0.0512 "
6. " " 2.....	0.053 "	0.0548 "
7. " " 2.....	0.053 "	0.0526 "
8. " " 3.....	0.032 "	0.0317 "
9. " " 3.....	0.032 "	0.032 "
10. " " "a".....	0.016 "	0.0177 "
11. " " "a".....	0.016 "	0.0174 "
12. " " C.....	0.021 "	0.021 "
13. " " A.....	0.129 "	0.129 "
14. " " A.....	0.129 "	0.129 "
15. " " A.....	0.129 "	0.127 <sup>2</sup> "
16. 2 gram steel No. 1 + 0.0173 gram. cryst. sodium phosphate.....	0.115 "	0.116 "
17. 2 gram steel No. 3 + 0.0231 gram cryst. sodium phosphate.....	0.132 "	0.133 "
18. } 1 gram cast iron.....	1.75	{ 1.743 "
19. } " " " ".....		{ 1.767 "
20. } " " " ".....		{ 1.761 "
21. } " " " ".....	1.79	{ 1.782 "
22. } " " " " dissolved in aqua regia ....		{ 1.755 "
23. } " " " " ".....		{ 1.743 "
24. } " " " " " as for steel.. ....		{ 1.750 "
25. } " " " " ".....		{ 1.745 "

<sup>1</sup> Determination by W. A. Noyes.

<sup>2</sup> With fresh, colorless, molybdic solution.

These determinations furnish, we believe, satisfactory proof that the method which has been described, secures a practically complete precipitation of the phosphorus, even when the amount present is only 0.02 per cent., and also that the ratio of phosphorus to molybdenum in the solution is constant and independent of the amount of phosphorus present; also that the ratio is not affected by the presence of silicon or arsenic in the solution. The cast iron used contains 0.84 per cent. of silicon. As regards arsenic, we have applied Marsh's test for arsenic to the yellow precipitate obtained from two grams of steel No. 2, and obtained only a very faint arsenic mirror, much fainter than that obtained under the same conditions, from 0.02 mgm. of arsenious oxide. If we suppose the arsenic to have been present in a compound analogous to the phosphorus compound, the molybdenum associated with it would correspond to only 0.0003 per cent. of phosphorus. The determinations with the cast iron also furnish evidence that the conversion of phosphorus into phosphoric acid is as complete by solution in nitric acid and oxidation with potassium permanganate as by solution in aqua regia and evaporation with nitric acid. The volumetric determinations with the cast iron are more accordant than the gravimetric. In view of the great difficulties known to exist in the way of securing pure magnesium pyrophosphate, we believe the volumetric determination will usually be found to be more accurate.

TERRE HAUTE, December 20, 1894.

## THE CONTRIBUTIONS OF CHEMISTRY TO THE METHODS OF PREVENTING AND EXTINGUISHING CONFLAGRATION.<sup>1</sup>

BY THOMAS H. NORTON.

Received December 24, 1894.

I have felt it desirable on this occasion to direct your attention to a brief review of the services which the chemist has thus far rendered in the battle with fire, to the field of investigation still open, to the methods of testing and experimentation in this branch, and to the application of fact already gained to American conditions. In the choice of this subject, I have, in common

<sup>1</sup> Abridged from the author's opening address before the Section of Chemistry of the American Association for the Advancement of Science, at the Brooklyn Meeting, August, 1894.

with some of my predecessors, left the domain of pure science to consider more closely certain economic aspects of chemistry, and enter, to some extent, into the province of chemical engineering, which is now recognized in our leading schools as entitled to distinct and separate treatment. A further reason which has influenced me is the practical absence, to this time, in our works of reference, of any attempt to collate and classify the knowledge gained in this field.

The total annual loss of insured property by fire is about \$200,000,000, and of this sum nearly one-half occurs in the United States,—\$90,344,075 in 1893. Foreigners marvel at this reckless disregard of the immense losses by fire shown by our countrymen, for from eighty to ninety per cent. of the 15,000 fires which occur annually, can be traced to easily preventable causes, and chiefly to faulty construction. Consider, for a moment, the tax which is being paid this Moloch. Our total loss of property amounts to one-fifth of the net profits of all the industries of the country. Propose to a trader or manufacturer coolly to throw one-fifth of the annual profits into the grate! Yet this is what our productive industries, as a whole, have been and are doing in an unconcerned, if not cheerful, manner. The direct loss by conflagration is, however, not the only factor. Our fire departments and water supply cost us \$30,000,000 annually; while the loss of wages to mechanics and other productive forces, and numerous contingent amounts, swell the actual total loss to a most serious sum. The fire department of London costs but one-third of that of New York City; and the same ratio applies to most European cities. During a residence of ten years in French and German cities, I saw the fire engines called out but five times; while the average resident of an American city is apt to witness a call at least once a week. England's annual fire bill is but little over \$10,000,000.

With these facts in view, is it not time to call a halt, to bring all the forces of science to bear in the battle, and redeem our America from what is nothing more or less than a servile bondage?

If we seek the reason for this vast difference in relative fire loss between the Europe of to-day and America, it is not to

be found in a superiority of facilities for extinguishing conflagrations. The equipment of American fire departments is far better than that of the fire departments abroad. It results simply from the fact that the European architect and builder have profited from the experience of the past, and learned that prevention is better than cure. The prevalent method of construction in New York is such, architects assure me, that the business part of the city awaits only the proper combination of circumstances to be the scene of a conflagration rivalling that of Chicago.

Before leaving these general considerations, it should be said that there are many hopeful indications of an awakening from this apathy, and ample recognition should be made of the earnest effort, inaugurated of late years in New England, to lessen fire risk; the application of the so-called slow-burning principle of construction, especially to factories. By the adoption of this principle it has been possible to reduce insurance rates from one and one-half to two and one-half per cent. down to two-sevenths of one per cent.

#### FIRE EXTINGUISHERS.

Passing to the more specific treatment of the subject, we find that, as in medicine, so in the matter of protection against loss by fire there are two distinct lines of action: prevention and cure, or the adoption of such measures as to render an outbreak of fire difficult, and a conflagration practically impossible; and the provision of the proper facilities for the rapid subjugation and limitation of fire under full headway. As in medicine, also, there is a growing conviction that the prophylactic treatment is the more important. It is hence particularly in this direction that the activity of the chemist has been chiefly called into play.

Let us first briefly review the methods of extinguishing fire.

In this field but little has been done to add to the efficacy of the agent used from time immemorial—ordinary water. In addition to its cheapness and universal distribution, water possesses, over other liquids, peculiar advantages for the purpose in view—high specific heat and the formation of a vapor which is non-poisonous. Sulphur dioxide has been used to some extent; in fact it is an old-fashioned method in European countries to

extinguish burning chimneys by kindling sulphur on the hearth. A quicker production of the gas is effected, more particularly for use in confined spaces, by introducing receptacles of burning carbon disulphide; and cylinders of liquid sulphur dioxide, have, under similar circumstances, been successfully employed. The advantage in the use of this gas consists entirely in its exclusion of the air necessary to maintain combustion. The slower diffusion consequent upon high density renders it superior for this purpose to other available gases. This advantage is, however, largely counterbalanced by its irritant, poisonous nature, and it has never been accepted as one of the recognized agencies of general application.

Of much greater value is carbon dioxide, the efficacy of which is likewise based upon its ability to prevent the access of air to the material in process of combustion. The ease with which this is accomplished is shown by the familiar experiments of our lecture courses in chemistry. For practical results in dealing with ordinary fires, it is found best to employ a highly charged aqueous solution of the gas. Such solutions as those prepared for use as a beverage, have frequently been used in emergencies. One large soda-water establishment has been able to extinguish several fires in its own factory and in the neighborhood by the prompt use of the carbonated water in its receptacles. A quick-witted pharmacist recently extinguished a serious fire in his store from benzene, by quickly using a pailful of soda-water drawn from his own fountain, the case being one in which simple water would have failed to accomplish the purpose.

The so-called chemical fire-engines, now regularly used in our public fire departments, are all constructed upon the principle of charging a quantity of water when used with carbon dioxide and ejecting a stream of the carbonated water by the pressure of the gas itself. In the size most frequently employed the supporting truck carries two cylindrical tanks of steel or copper, holding about eighty gallons of water and twenty-eight pounds of sodium bicarbonate with a leaden jar containing fourteen pounds of sulphuric acid. At the moment of using, by a simple mechanical device, the acid is admitted to the solution and a pressure of 140 pounds to the square inch is developed. The

tanks are charged alternately while in operation so that it is possible to maintain a continuous jet of one-fourth of an inch. The whole apparatus is light and easily drawn by two horses. There is also in use a combined manual and chemical fire engine devised by Foster. The pumps fill, with water, the compartments in which the chemicals are dissolved and whence the solutions come together in a generating chamber where the gas is evolved. Such engines are capable of throwing per minute thirty gallons of water containing 250 gallons of carbon dioxide to a distance of ninety feet. This type is also arranged for connection with high pressure mains. Very careful tests carried out in 1883 showed conclusively the great value of a small quantity of carbonated water in extinguishing fierce flame, especially in a confined situation and when combustion had not penetrated much beneath the surface. The same principle was applied earlier by Baragwanath and others in a variety of forms, to portable extinguishers. Dick's extinguisher, largely used in England, is a cylindrical tank of seven gallons, easily carried on the back, giving a pressure of from 70 to 120 pounds, and possessing a projectile range of fifty feet. The peculiar feature of this type is the storing of the sulphuric acid in a glass container, which is easily broken when the apparatus is to be used. Zabel's apparatus, like Dick's, is charged with sodium bicarbonate, but the acid used is contained in a cylinder from which it is liberated by simple inversion. Devices, essentially the same, have been introduced by Masnata and VanWisker. In Carter's extinguisher the sulphuric acid is replaced by tartaric acid.

Platt's extinguisher has been successfully used for many years, and is valued on account of its simplicity; the turning of a valve and the inversion of the apparatus bringing it at once into operation. Other efficient extinguishers of American origin are the Babcock, the Harkness, and the "Climax." In the latter, sulphuric acid is replaced by oxalic acid, and in both the Harkness and "Climax" the carbonated solution is forced out by a pump. The Babcock extinguisher is filled with a solution of sodium bicarbonate, and has in its upper part a vessel of acid suspended by lateral pivots to a stirrup depending from the top of the apparatus. The stopper of this vessel is worked by a rod

through the top of the extinguisher. By withdrawing the stopper, the vessel tilts over and mingles the acid with the solution producing at once the necessary pressure.<sup>1</sup>

The most recent and perhaps most efficient of chemical extinguishers is that introduced in 1893 by Dr. Henry P. Weidig, and extensively tested throughout our country during the past twelve months. It is adapted not only for portable use, but also for replacing ordinary town engines and for permanent installation in factories and on board ships, etc.

The apparatus consists of a steel vessel containing liquid carbon dioxide so arranged that it may be brought in connection with a receptacle filled with carbonated water, or a solution of ammonium carbonate, under any desired pressure. The carbonated water meets in its exit pipe with a stream of ammonia gas emanating from a cylinder of liquid anhydrous ammonia. The carbon dioxide is thus bound in the form of a soluble salt, ammonium carbonate. The solution thus formed is forcibly ejected, and, on reaching a fire, the heat not only volatilizes the water but decomposes the salt, so that a mixture of steam, carbon dioxide, and ammonia is the result. One volume of water will yield under these circumstances twenty-five volumes of the two latter gases.

The principle of rapidly filling a confined space where fire has broken out with inert gases has been extended to the use of the gaseous products issuing from the combustion under boilers. In certain industrial establishments devices are introduced by which the current of the mixture of nitrogen, carbon dioxide, and aqueous vapor can be directed, at will, into a given apartment. The results are quite effective, combustion being promptly and permanently stopped. Other additions than carbon dioxide to the water used in extinguishing fires have proved of doubtful utility when submitted to practical tests. The list of such proposed additions includes potash (Kaiser), clay (Glaser), a mixture of sodium sulphite, and four parts sodium alum (patented 1884 in Austria, by Trotha, and sold in the form of cartridges), salt, alum, waterglass, copperas, Glauber's salt, borax, magnesium chloride, sodium phosphate, and soda.

<sup>1</sup> Hexamer, *Journal of the Franklin Institute*, August, 1885.



Ammonia gas alone has been recommended. Its lightness and irritant properties render it, however, much less efficient than carbon dioxide or sulphur dioxide.

Hand grenades,<sup>1</sup> consisting of glass bottles, usually of a spherical form, charged with aqueous solutions of various chemicals, have found their way of late years into somewhat extended use. They are conveniently arranged in the corridors of large buildings, and are intended for use in extinguishing incipient outbreaks of fire. The grenade is to be thrown with such force into the center of combustion that it breaks and scatters its contents upon the burning material. The salts present are supposed to act by either giving off incombustible gases or by incrusting the burning articles, thereby excluding air. In practice, however, it is found that these grenades render but slight service, as they are frequently unbroken when thrown, especially against non-resistant substances. They are supposed to be charged with strongly carbonated water, or with a saturated solution of ammonium chloride, sodium chloride, sulphite, or thiosulphate. Analysis, however, shows quite a variety of composition in the contents. Sir Frederick Abel,<sup>2</sup> in 1881, found one to contain a strong solution of salt and waterglass. Geissler examined three current types with the following results:<sup>3</sup>

*Hayward's Grenade*.—Gross weight 1,120 grams; weight of liquid, 750 grams; composition, an aqueous solution of 15.7 per cent. calcium chloride and 5.6 per cent. magnesium chloride.

*Harden's Grenade*.—Gross weight, 900 grams; weight of liquid, 555 grams; composition, an aqueous solution of 19.5 per cent. sodium chloride, and 8.9 per cent. ammonium chloride.

*Schonberg's Grenade*.—Gross weight, 770 grams; weight of liquid, 440 grams; composition, an aqueous solution of 1.66 per cent. sodium carbonate, and 6.4 per cent. sodium chloride.

It may be noted in passing that the salts in these grenades cost about one per cent. of their selling price.

Finally, mention should be made of extinguishing powders,<sup>4</sup> the use of which is literally a fighting of fire with fire. They

<sup>1</sup> Hexamer, *loc. cit.*

<sup>2</sup> Amer. Arch, 13 and 14.

<sup>3</sup> Pharm. Centrbl., 1885, 447.

<sup>4</sup> Hexamer, *loc. cit.*

are well devised to produce, by rapid combustion at the expense of the oxygen in saltpeter, a sufficient volume of inert gas—chiefly sulphur dioxide and carbon dioxide—to prevent the circulation of air about a fire, and thereby cut off the supply of atmospheric oxygen for further combustion. Their application is, of necessity, limited to small enclosed spaces without many openings for ventilation, and they have been found chiefly valuable in drying rooms where easily volatile products are being driven off, as in connection with the manufacture of oilcloth. The ingredients are coarsely powdered and readily ignited. They are often packed in cartridges and provided with fuses. They burn without explosion, with a bright white flame, a strong odor, and much smoke. Each pound yields about four and eight-tenths cubic feet of gas, which consists of two and three-tenths sulphur dioxide, one and one-tenth parts carbon dioxide, and one and four-tenths parts nitrogen. One pound should be used for every 240 cubic feet of an enclosed space. The composition of the best known of these powders is as follows:

<i>Bucher's powder</i>	{	KNO <sub>3</sub>	60 parts.
		S	36 "
		C	4 "
<i>Heeren's powder</i>	{	KNO <sub>3</sub>	63 parts.
		S	29 "
		C	4 "
		Fe <sub>2</sub> O <sub>3</sub>	4 "
<i>Schweizer's powder</i>	{	KNO <sub>3</sub>	58 parts.
		S	36 "
		C	3 "
		Fe <sub>2</sub> O <sub>3</sub>	1½ "
		SiO <sub>2</sub> (sand)	75 "
<i>Gruneberg's powder</i>	{	KCl	20 parts.
		KNO <sub>3</sub>	50 "
		S	50 "
		MnO <sub>2</sub>	1 "
		Rosin	10 "
<i>Zeisler's powder</i>	{	KNO <sub>3</sub>	60 parts.
		S	36 "
		C and CaO	4 "

<i>Johnston's powder</i>	{	Equal parts of KCl, KNO <sub>3</sub> , MnO <sub>2</sub> , and Rosin, moistened with waterglass and pressed into briquettes.
<i>Phillips' Fire Annihilator</i> (introduced in 1851.)	{	KNO <sub>3</sub> 60 parts. C                        20 " CaSO <sub>4</sub> + 2H <sub>2</sub> O    5 "

This latter was pressed in the form of a hollow brick. The central cavity contained sugar, and potassium chlorate and a vial of sulphuric acid, the latter so arranged as to be easily broken by a simple mechanical device. The brick was usually placed within a double cylindrical receiver containing water, so that the ignition of the powder caused not only the evolution of a large volume of gas, but also, by its heat, a liberation of a considerable amount of aqueous vapor.

In reviewing this portion of our subject it would appear that but few opportunities are afforded the chemist for further contributions of value. It would seem advisable, however, to study the feasibility of extending the use of carbon dioxide along lines similar to those in which automatic sprinklers have found such satisfactory application. In many factories and in numerous stores and warehouses the sprinkler, while most effective in quenching flame or hampering its progress, causes serious damage to manufactured products or materials for manufacture. The advantages of carbon dioxide over water under these conditions are manifest. It is not difficult to conceive of a system of piping, opening naturally at the level of the floor, through which either automatically or under the control of a watchman, a powerful current of the gas could be directed into any apartment where flame was apparent. In the many cases where the losses by water do and would naturally far exceed the losses by direct combustion, there is but little doubt that the use of the invisible, inert, harmless gas would enormously limit the destruction of valuable property.

We come now to the most important division of our subject ; namely, the methods of preventing loss or suffering by fire through the use of structural materials, textile fabrics, and the like, which are either entirely incombustible or slowly combusti-

ble or from which the property of rapid combustion has been largely removed by special treatment. A structure built entirely of stone, brick, iron, cement, etc., is an illustration of the first type. A structure of brick with heavy beams of wood, heavy floors of plank, no hidden air-spaces, and a general absence of the lighter forms of woodwork, illustrates the second type,—the slow combustion construction. The third type is to be found in an edifice of wood, the component parts of which, either by impregnation or by suitable coatings, have lost the property of ready inflammability.

The study of the choice of materials and their most efficient grouping as employed in the first and second methods of construction, apart from architectural considerations, falls purely within the domain of the mechanical engineer. It involves the question of strains and stresses under ordinary conditions and under the conditions of an elevated temperature.

It is in the special field of rendering such easily combustible substances as wood and the vegetable fibers used in textile fabrics more or less resistant to flame that the chemist has been able to render service.

Could our methods of building be limited to the completely fire-proof or the slow-burning system of construction, and interior decoration and equipment be restricted to the use of non-combustible materials, it is evident that the chemist would have but little to do. But mechanical considerations, canons of taste and questions of outlay will, for a long time to come, sustain the extended use of wood in the erection and finishing of many classes of edifices, especially of our homes. The beginnings of our towns and cities are almost entirely in wood, and the same may be said of the suburbs of our centers of population. It will be many years before the rural residence and the home of the laborer in America will be as universally constructed of non-combustible materials as in Great Britain, France, Germany, and other European countries. In such a country as Japan it is almost impossible to imagine any general departure from the time-honored and picturesque national construction of bamboo. The restriction of fabrics to fibers of animal origin is likewise out of the question.

In noting the historical development of the work of the chemist in the field as above outlined, we will first consider the methods which have been applied to textile fabrics and paper, and next those which have been used to render wood uninflammable.

#### TREATMENT OF TEXTILES AND PAPER.

The first experiments in this direction were made in England in 1735 by Obadiah Wild,<sup>1</sup> who secured a patent for rendering the cartridge cases used by the navy resistant to flame. This process consisted of the addition of a mixture of alum, borax, and copperas, to the paper pulp employed. Early in the present century the subject attracted the attention of several chemists. De Hemptine, of Belgium, in 1821, made quite an extended study of mixtures, similar to that of Wild, and other substances. At the same time Brugnatelli recommended the use of potassium silicate, Hermstadt of ferrous sulphate, De Lisle of an unnamed compound.<sup>1</sup> Gay Lussac<sup>2</sup> was deeply interested in the subject. In 1830, as the results of his experiments, he recommended the use of various chlorides, phosphates, borates, tartrates, and carbonates without, however, considering the difficulties involved in their application on a large scale. The employment of the alkaline carbonates was later urged strongly by Prater, while Fuchs<sup>1</sup> and Bethel in 1838 advocated waterglass and others, gypsum. Several patents were taken out during this period by the different investigators. Still later Chevalier recommended the use of a mixture of borax and ammonium sulphate. The use of ammonium sulphate alone was proposed by De Breza in 1838, and that of ammonium chloride by Froggant in 1857. In 1855 M. Solomon,<sup>2</sup> of Paris, submitted to the English Board of Ordnance a process for rendering canvas uninflammable. It consisted of immersing the materials for a day in each of the following baths:

I. Aluminum sulphate, 30 parts. II. Dry calcium chloride, 20 parts

Glue (gelatin),	10 "	Glue,	10 "
Water,	60 "	Water,	70 "

<sup>1</sup> Versmann and Oppenheim, Report to the British Association, 1859

<sup>2</sup> *Ann. chim. phys.*, 18, 211.

<sup>3</sup> *Amer. Arch.*, 13 and 14.

[TO BE CONTINUED.]

## THE ACTION OF ORGANIC AND MINERAL ACIDS UPON SOILS.

BY HARRY SNYDER.

Received January 2, 1895.

IN soil analysis, the hydrochloric acid use for dissolving the potash, lime, and phosphates has a specific gravity of 1.115. This acid is used because it is supposed to represent, practically, the same solvent power which agricultural plants possess in obtaining their food from the soil. Inasmuch as this premises is the foundation of a part of the present system of soil analysis, it is a question of the greatest importance. One of the indications which points to the truth of the premises is the similarity of the action of hydrochloric acid of this strength, and of organic acids upon samples of soil.

*Organic Acids.*—In some of the soil work which has been in progress in the chemical laboratory of the Minnesota Experiment Station, the solvent action of the various organic acids has been determined with another ultimate object in view. Incidentally, the results give sufficient data for the comparative action of the organic acids and of hydrochloric acid, sp. gr., 1.115, upon the same samples of soil.

Different types of soil are acted upon quite differently by the various organic acids, and general conclusions regarding their action upon various types of soil can not be stated. Hence the statements which are made upon this question have reference only to the type of soil under consideration.

The figures given in the table were obtained from a soil sample taken from one of the rotation plots at the Experiment Station. In obtaining the solutions for analysis, oxalic, tartaric, and citric acids, of ten per cent. strength, by weight, were used. The digestion was carried on for thirty-six hours in the Snyder soil flask as used at this station. The organic acid mixture was made by preparing a ten per cent. solution, by weight of citric, oxalic, and tartaric acids. The material soluble in the organic acids was separated by filtration and washing. The solution was then gently ignited to remove the organic acids, so that the analysis could be completed in the usual way.

Ten per cent. solutions were used because the more concentrated ones crystallized upon standing, and, then too, preliminary trials indicated that the more concentrated organic acid solutions possessed less solvent power than those here used. One difficulty experienced in the work was obtaining tartaric acid free from potash, and citric and oxalic acids free from lime. All of the determinations were made in duplicate, and controlled by blank determinations.

TABLE I.

## SOLVENT ACTION OF HYDROCHLORIC AND ORGANIC ACIDS UPON A SOIL.

	Hydrochloric acid 1.115 sp. gr.	Ten per cent. solution of			
		citric acid.	oxalic acid.	tartaric acid.	organic acid mixture.
Total insoluble, per cent....	84.08	87.90	85.07	87.67	85.93
Potash.....	0.30	0.12	0.18	0.06	0.10
Soda.....	0.25	0.17	0.19	0.05	0.12
Lime.....	0.51	0.50	0.23	0.41	0.45
Magnesia.....	0.26	0.27	0.21	0.32	0.33
Iron oxide.....	2.56	1.59	1.14	1.62	2.23
Alumina.....	4.24	1.45	3.96	1.77	2.99
Phosphoric anhydride.....	0.23	0.26	0.14	0.11	0.26
Sulphuric ".....	0.08	0.10	0.05	0.06	0.05

The oxalic acid caused an increase in the solubility of the alumina. There is a marked difference between the solvent action of these three acids. The oxalic acid possesses the greatest solvent action upon the complex insoluble matter of an alkaline nature. The citric acid possesses the greatest solvent action upon the lime, magnesia, and the sulphuric and phosphoric anhydrides. The amount of lime dissolved by the oxalic acid is greater than would, at first, be expected, but the complex nature of the solution, and the presence of the salts of other metals, has caused nearly half as much lime to be dissolved by the oxalic acid as by the hydrochloric acid of sp. gr. 1.115.

The ten per cent. mixture of the three organic acids has resulted in dissolving as much phosphates and magnesia, and nearly as much lime as any one of the acids acting alone. The potash does not appear to be as soluble in the organic acid mixture as the other elements of plant food.

The amount of potassium, iron, and aluminum oxides, dissolved by these three organic acids and their mixtures is somewhat less than that dissolved by the hydrochloric acid. The

iron and alumina are not of any economic importance in interpreting the results of soil analysis. The main difference between the solvent action of the hydrochloric and the organic acids is in the somewhat smaller amount of potash dissolved by the organic acids.

With the exception of the solubility of the potash, as noted, these results bring out, in a general manner, the value of hydrochloric acid of 1.115 sp. gr. as a solvent, over the organic acids, of ten per cent. strength, because the hydrochloric acid represents the limit of the solvent action reached by any one of the organic acids acting alone or in a mixture.

For the purpose of comparison, the solvent action of hydrochloric acid, sp. gr. 1.115, and the maximum limit reached in any case, by the organic acids, are given, together with the name of the acid possessing the highest solvent power for that constituent.

TABLE II.

	Hydrochloric acid, sp. gr. 1.115.	Largest amount dissolved by organic acids.	Name of the organic acid.
Total insoluble, per cent.....	84.08	85.07	Oxalic
Potash.....	0.30	0.18	Oxalic
Soda.....	0.25	0.19	Oxalic
Lime.....	0.51	0.50	Citric
Magnesia .....	0.26	0.27	Citric
Iron oxide.....	2.56	2.23	Mixture
Alumina .....	4.24	3.96	Oxalic
Phosphoric anhydride.....	0.23	0.26	{ Citric and Mixture
Sulphuric " .....	0.08	0.10	

*Mineral Acids.*—The action of the concentrated mineral acids upon the same sample of soil is given in Table III. Concentrated hydrochloric acid, forty per cent. strength, dissolved two and a quarter per cent. more of the complex silicates than nitric acid of the same strength. Concentrated nitric acid possesses a stronger solvent action than the dilute hydrochloric acid. The concentrated hydrochloric acid dissolved somewhat more potash than the hydrochloric acid of 1.115 sp. gr. The amount of lime, phosphates, and sulphates, dissolved by the concentrated hydrochloric acid, was about the same as when the more dilute acid was used; the concentrated acid, however, dissolved more of the complex silicates of potash, iron, and alumina. Sulphuric acid possesses the strongest solvent action.



Of the total potash in the soil, as determined by fusion, less than eighteen per cent. is soluble in the hydrochloric acid as used in soil analysis; about ten per cent. is soluble in oxalic acid, and three per cent. in tartaric acid.

TABLE III.

	CONCENTRATED ACIDS.			
	Hydrochloric acid.	Nitric acid.	Sulphuric acid.	Total by fusion methods.
Total insoluble, per cent.....	81.20	83.45	80.45	72.45
Potash.....	0.42	0.30	0.52	1.75
Soda.....	0.31	0.18	0.40	0.50
Lime.....	0.55	0.30	0.53	0.86
Magnesia.....	0.40	0.32	0.52	0.72
Iron oxide.....	3.41	2.97	3.57	3.63
Alumina.....	5.84	4.55	6.88	12.71
Phosphoric anhydride.....	0.23	0.23	0.26	0.28
Sulphuric ".....	0.08	0.08	0.10	0.10

## NEW BOOKS.

A TREATISE ON INDUSTRIAL PHOTOMETRY, WITH SPECIAL APPLICATION TO ELECTRIC LIGHTING. BY A. PALAZ, PROFESSOR OF INDUSTRIAL ELECTRICITY IN THE SCIENCE FACULTY OF THE UNIVERSITY OF LAUSANNE. TRANSLATION BY GEO. W. PATTERSON, JR., ASSISTANT PROFESSOR OF PHYSICS IN THE UNIVERSITY OF MICHIGAN, AND M. R. PATTERSON. pp. 322. New York: D. Van Nostrand Co., 1894. Price, \$4.00.

Many of the methods of photometry which have been long in use for measuring the intensity of light from gas flames have required modification when applied to the measurement of the intense light produced by electricity. A book which gathers together and arranges, systematically, the work on the subject which is scattered in many different journals, and which is frequently difficult of access, will be very welcome to many who are interested in the subject.

The first part of the book gives a discussion of the general principles of photometry and includes a description of all of the common photometers and photometric standards. This part of the book is quite full and will be of value to anyone interested in photometry in any of its applications. Then follow chapters on the equipment of photometric laboratories, and on the measurement of the intensity and distribution of light from electrical sources.

In an appendix of eight pages the translators criticise or give additional information upon a few topics in the book.

The work of translation appears to have been carefully done, and the English used by the translators is good. A short index is given, which might be made more comprehensive with great advantage. There are a great many short references to particular topics, and to the work of individuals, which can not be found by means of the index.

W. A. NOYES.

**DESCRIPTIVE INORGANIC GENERAL CHEMISTRY. A TEXT-BOOK FOR COLLEGES.** BY PAUL C. FREER, M.D., PH. D., (MUNICH), PROFESSOR OF GENERAL CHEMISTRY AND DIRECTOR OF THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF MICHIGAN. Revised edition. pp. 550. 54 Illustrations. Boston: Allyn and Bacon. 1894. Introductory price \$3.00.

This book is intended as a text-book for colleges and is therefore adapted for the use of students who already have some knowledge of the elementary principles of the science. The treatment of the subject is consequently somewhat different from that usually pursued in the best of the recent text-books on chemistry. For example the book begins with a discussion of the atomic theory and the composition of chemical compounds. The author believes that "beginners should be taken through a course in which only a few elements and compounds are discussed, with the purpose of familiarizing the pupils with the fundamental laws which govern chemical change." "During the progress of such work as this," he continues, "I would not advise the use of chemical symbols or any reference to the atomic theory. It is manifestly impossible to make a student without experimental knowledge, understand, in all its bearings, a theory which it has taken some ninety years to place upon its present footing. If an elementary course, in which every stated fact has been proved by actual experiment, precedes the work given in this book, the pupil will be then amply fitted to look at chemical phenomena from the basis of the atomic theory."

Professor Freer is undoubtedly right in this matter and the sooner the teachers of chemistry in this country recognize the truth contained in the above-quoted statements and model the instruction on the plan there suggested the better it will be for the teaching of the science of chemistry in our colleges and un

versities. If the teaching of the elements of the subject could be relegated to the secondary schools, where it properly belongs, then it would be possible to give a very much more satisfactory course in chemistry in our colleges and universities on the lines laid down by Dr. Freer in the present book.

In the descriptive part of the work the author has used the last editions of Graham-Otto's "*Lehrbuch der Allgemeinen Chemie*," and Ladenburg's "*Hardwörterbuch der Chemie*," though the original articles in the chemical journals have been freely consulted. The elements have been discussed, in general, in the order in which they occur in the periodical system and the attempt has been made to show the influence exerted by the nature of the elements which form a chemical compound.

The book must be regarded from all points of view as a very good one and one that can be highly recommended for use in our colleges and universities. The facts are stated clearly, concisely, and correctly, and the latest information obtainable on the subject is always presented. Teachers of chemistry will find the book full of new ideas and suggestive of the relations of the various phenomena to one another that are usually overlooked in the ordinary text-book on the subject.

What the author has to say on the subject of valence in the preface to the book is very interesting. He says: "My views upon the subject of valence and the use of structural formulas may probably be regarded as too conservative by many of my colleagues, but I have been led to adopt these views by the growing conviction that the dogmatic use of supposed laws of valence and of constitutional formulas founded upon very incomplete experimental evidence, is causing more harm than good to the advancement of chemical science." Most of the teachers of chemistry will endorse the latter part of this statement. The author has made free use of the facts derived from the domain of the so-called physical chemistry wherever he has thought it advisable, and he has thus been able to present reasons for our views of certain chemical phenomena which would be otherwise perfectly inexplicable to the student.

Notwithstanding the general excellence of the book it has some minor faults. The use of the word not-metal throughout

the work when the word non-metal is in general use by chemists seems ill-advised and unwarranted. The same statement may be made also with reference to the word not-conductor. Hydroiodic acid and stibional are used instead of the more usual hydriodic acid and antimonyl and for no apparent reason. Hydrazine, hydroxylamine, azoimide, and methine are written without the final *e* probably because that is the German way of spelling these words and the author is more familiar with them in German than in English. No reference whatever is made to the preparation of the diamond artificially by Moissan and, in speaking of the preparation of the acid  $\text{HN}_3$ , the simplest and best method of all that have been proposed, *viz.*, that of Wislizenus, by the action of nitrous oxide on sodium amide, is entirely omitted.

On page 278, near the bottom, occurs the following remarkable statement: "By a judicious combination of the iodides of organic radicles, carbon and hydrogen compounds containing as many as sixty *carbonates* in a molecule have been prepared." In a foot-note, Hill and Hägele are made responsible for this "judicious combination," but it is doubtful if these chemists would recognize their own statement in this form.

$\text{HN}_3$  is referred to as azoimide or hydrogen nitride and the salts of the acid are called nitrides. It would seem to the reviewer that a name which recalled the fact that the substance was an acid, would be preferable, and, since there are quite a large number of nitrides known which are certainly not salts of the acid  $\text{HN}_3$ , much unnecessary confusion will be introduced by the use of the word nitride for a salt of the acid  $\text{HN}_3$ . These are, however, but slight faults which may be readily corrected in the next edition of the book and that another edition of so excellent a work will soon be called for seems highly desirable and also highly probable.

The book is singularly free from typographical errors, is well printed and well bound, contains a useful appendix of laboratory notes intended as a guide to teachers and students in compiling a list of experiments, and last, but by no means least, a very complete index.

W. R. ORNDORFF.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

---

### THE SYNTHETIC FOOD OF THE FUTURE.<sup>1</sup>

BY HARVEY W. WILEY.

THE problem of human nutrition is the great groundwork of sociology. I use the word nutrition in its broadest sense, including clothing and fuel, which, while not as essential as food to life, are quite as important factors in civilization. Until within a few years the study of nutrition and the means of providing it have been deemed the exclusive function of agriculture. In the development of this idea, we have seen springing into existence in all parts of the civilized world, within the past twenty-five years, colleges of agriculture and agronomic experiment stations in large numbers. Especially in this country have we seen the greatest activity in this line. In all the states and territories, fostered by the federal government, schools have been established in which instruction in agriculture has been made a fundamental branch of the college curriculum. There are fifty-seven agricultural experiment stations in the United States. Each state and territory has at least one. Louisiana has three, Alabama, Connecticut, Massachusetts, New Jersey, and New York each two, and the Department of Agriculture two, one in Florida and one in California. For the support of the state and territorial stations, Congress has made an appropriation for the fiscal year ending June 30th, 1895, of \$745,000 and for the Department stations \$10,000, in all \$755,000. The agricultural colleges in the states and territories have also been endowed by

<sup>1</sup>Retiring Address of Harvey W. Wiley as President of the Society, Boylston Hall, Harvard University, Dec. 28, 1894.

grants of public land proportionate in extent to the numbers of senators and representatives in congress. The annual money value of these grants varies with their extent and the wisdom with which they have been invested, but the total sum is approximately a million and a half dollars. In addition to this a sum of money is granted annually to each agricultural college directly from the treasury, and this sum is to be increased at the rate of \$1000 per annum until it amounts for each institution to \$25,000 a year. This amount will be reached in five years. At present the total sum so granted is nearly a million dollars, and it will soon be a million and a quarter. The total amount of the financial aid thus granted directly from the treasury to the agricultural colleges and experiment stations is at the present time approximately three million and a quarter dollars annually. To this must be added the amount given directly by the states and arising from private endowments—a sum of no inconsiderable importance. In all it may be said that about four million dollars in this country are annually devoted to the promotion of agricultural and allied education and research, a sum more liberal than that devoted by any other country to similar objects.

The natural result from such investigations is an increase in soil productiveness, the reclamation of lands supposed heretofore to be unfit for tillage and a greater economy of food production. The supply of human food, therefore, appears to more than keep step with the increase in population and food consumption. In so far as economic reasons extend, there is no occasion to look outside of scientific agriculture for the supply of human food.

But another view is presented of the subject of a more strictly scientific aspect, based on the remarkable progress which has been made in the past few years in the domain of synthetic chemistry. The year 1828 marks a new era in the history of chemistry. It was in this year that Wöhler succeeded in making synthetic urea by the union of cyanic acid and ammonia. Urea is not of a high order of organic bodies; in fact, it is a result of retrograde action in the living organism and the consequent result of the breaking down of higher organic bodies; yet its artificial formation was a brilliant victory of chemical methods, a bold and successful charge

on the breastworks of organic compounds. To change the figure, it was the crossing of the dead line which had been drawn previously between the living cell and the inanimate crucible. The line once having been crossed, the old distinctions between the organic and the inorganic world have been completely obliterated. With them have gone also the divisions which were supposed to separate the animal from the plant. It is now known that animals do not get their entire nourishment from so-called organic nor plants from inorganic compounds. Many plants, especially those free of chlorophyl, live alone on organic compounds. Especially noteworthy among these, from the character of the chemical activity which they manifest, are the vegetations of a bacterial nature, living largely on organic products. Even the green plants first fabricate the inorganic elements into organic compounds before taking them into their tissues. The green cells are the tiny kitchens in which the meals of the plant molecules are prepared.

Without dwelling on further details of this subject, it is sufficient for the present purpose to state that the progress of modern science has entirely changed our ideas respecting the sharp lines of division which were formerly thought to exist between the animal and vegetable, and between the nature of artificial chemical compounds and those produced by biochemical action in the living organism. We stand, therefore, face to face with the fact that it is possible to produce, by artificial means in the laboratory, compounds which have heretofore been the results of exclusive biochemical functional activity of living organisms.

One remarkable fact in connection with Wöhler's synthesis of an organic compound is of interest here. While all the chemical world wondered at Wöhler's achievement, nearly fifty years elapsed before this rich field of chemical progress was further cultivated to any extent, with the single exception of the synthesis of acetic acid by Kolbe, in 1845. But since that time remarkable progress has been made. It is not my purpose here to recite in detail the synthetic accomplishments of Berthelot, Kekulé, Kolbe, Maumené, Baeyer, Hoffmann, Frankland, Ladenberg, Fischer, and many other celebrated workers in this field.<sup>1</sup>

<sup>1</sup> See *Rise and Development of Organic Chemistry*, by C. Schorlemmer, revised edition, 1894.

For the purpose of the present paper, only two points in organic chemical synthesis need be considered; *vis.*, first, the economy of the process, and second, the probability of the production of food compounds suited to the nourishment of man.

In respect of the first point, we find many illustrative examples of synthetic products which are furnished at so small an expense as to practically exclude from the market the corresponding natural articles. Among these may be mentioned salicylic acid made artificially by Kolbe's process. Salicylic acid occurs as a natural product in the flowers of *Spirea ulmaria* and as a methyl ether in the oil of wintergreen (*Gaultheria procumbens*). It can be formed by synthesis in various ways, as, for instance, by fusion of salicylaldehyde with potassium hydroxide. Salicine, coumarine, indigo, cresol, or toluenesulphonic acid may be substituted for the salicylaldehyde. When phenyl carbonate is heated with a caustic alkali, salicylic acid is also produced. It may also be obtained when an alkaline solution of phenol is boiled with carbon tetrachloride. But none of these processes, although of great interest chemically, have any value commercially save that of Kolbe, or more properly, Kolbe and Lautemann, which consists of passing carbon dioxide into sodium phenylate.

But it will be observed that the phenol which is the base of the process, is itself an organic compound, or the result of the destructive distillation of an organic compound produced by nature. It is not impossible to produce phenol by artificial synthesis. It is said that by surrounding the points of an electric arc light with hydrogen that carbon and hydrogen combine to form acetylene,  $C_2H_2$ . According to Berthelot,<sup>1</sup> fuming sulfuric acid absorbs acetylene and the product so formed fused with caustic soda forms phenol or sodium phenate. But it needs no further illustration to show that a phenol formed in this manner could never, on account of its great cost, be used for the commercial manufacture of salicylic acid.

A distinction should be made in this matter between the formation of possible food products by synthesis from existing organic natural bodies, and the synthesis which begins with the inorganic elements themselves. The transformation of one organic

<sup>1</sup> *J. prakt. Chem.*, 2, 10, 93.

<sup>2</sup> *Compt. rend.*, 68, 539.



body into another of greater value to human industry is quite a different matter from the building up of organic bodies without the help of a living organism. Berthelot himself, who is now the apostle of synthetic foods, summarizes the steps which will probably be traversed on the way which is to end in the substitution of the chemist for the farmer :

1. Hydrocarbons, obtained by the union of hydrogen and carbon.
2. Alcohols formed from the hydrocarbons in various ways.
3. Aldehydes and acids obtained from alcohol by oxidation.
4. Amides produced by the action of ammonia on the alcohols.
5. Alkaloids formed by the action of ammonia on the alcohols and aldehydes.

But even granting the fullest development of such a scheme, the impartial observer will be compelled to admit that there is still an immense gulf between the best of the products formed and human food.

In the case of medicines and drugs, perhaps the case is more hopeful. In so far as mere transformation of one organic substance into another of greater therapeutic value is concerned, much progress has already been made. But in nearly all of these cases the products are obtained by the splitting up of more complex into less complex molecules. In other words, it is a retrograde synthesis and not a constructive one. A mere list of remedies in common use, which have been formed in this way, would form an extensive index of pharmacy.

Both Liebig and Wöhler, as early as 1837, foresaw this advance in synthetic chemistry and predicted the synthesis of alkaloids and antiseptics and even of sugar.

Founded on the classical researches of Williamson on etherification has been built the art of forming by synthesis a great variety of flavoring matters for food and drink. In the strict sense of the term, these condiments are not foods inasmuch as they are not subject to digestion and do not take any part in the nourishment of the tissues. They have a nearer relationship, however, to the purpose of this address than the bodies already mentioned.

The slow natural oxidation of the alcohols in fermented and dis-

tilled drinks, giving rise to ethers of delicate odor and flavor, is an expensive process, and synthetic chemistry has boldly come to the aid of nature. The essences of fruits and flowers are now elaborated in great numbers in our laboratories and supply to a certain extent the natural products. With the aid of ethyl alcohol, burnt sugar, and a collection of artificial essences, the skillful manipulator will mix, in short order, drinks which resemble bourbon and old rye, madeira and sherry. The pure fruit flavors of many soda-water fountains could easily prove an alibi in respect of orchards. In the great majority of cases these essences are also the products of retrograde synthesis, or have for the base of manufacture an alcohol derived from the fermentation of a natural sugar. While it is true that they can be manufactured at a lower cost than attends their natural production, and while they are used as condiments in foods and drinks, yet in no sense can they be regarded as a step toward the preparation of foods from inorganic elements by purely chemical means. The principal artificial flavoring extracts are the derivatives of the fatty acids, especially the ethers and aldehydes. The ethereal salts of acetic, valerianic, benzoic, salicylic, and butyric acids, are the most common of these bodies. Methyl, ethyl, and amyl are the bases most usually found in the above compounds. Vanillin has also been made synthetically. Analysis showed that this natural product of the vanilla fruit was methylprotocatechuic aldehyde. This knowledge led to its artificial production. From turpentine is derived a perfume turpineol which is known as "lily of the valley." The artificial production of musk and of the perfume of the violet have also been accomplished.

Whether or not these bodies are injurious to health is a question whose discussion can not be entered into here. In the case of one of the best known of these condiments, and one which is not of ethereal origin, it may be said that its use in foods is prohibited in some countries, whether it be used as a sweetener or as an antiseptic. In justice to saccharin, however, it should be stated that repressive legislation against it has been quite as much due to a feeling of jealousy on the part of beet-sugar producers as to a suspicion of unwholesomeness on the part of the medical fraternity. Certain it is, however, that, even as a sweet-

ener, it will never take the place of sugar and because of its anti-septic properties it must necessarily interfere to some degree with the action of the digestive ferments.

It is not necessary to take up in detail other synthetic compounds which have attained a commercial success. The artificial dye stuffs are types of these bodies and illustrate, in a most brilliant manner, the progress of chemical synthesis based on the knowledge of the internal constitution of organic compounds derived from analytical investigations. But even the most enthusiastic believer in the future triumphs of chemical science will fail to find anything more than an inspiration in these achievements in respect of the production of foods. In all cases of coloring matters, original organic compounds derived from living cells, or the products of their destruction, have served as the bases of the processes. Without an elaborate review of this field therefore, and which, moreover, has already been made,<sup>1</sup> we pass at once to consider these achievements in synthesis which relate directly to the matter under consideration.

Along two lines of especial interest to food production, synthetic chemistry has made its greatest advances; *viz.*, the production of glycerides and of sugars. Wurtz<sup>2</sup> has described a method of synthesizing glycerol, which, in logic, would be called arguing in a circle.

	HCHBr
Tribromhydrine,	CHBr, is decomposed with silver
	HCHBr

acetate forming triacetine. This is saponified by baryta yielding glycerol. The tribromhydrine, however, is first prepared from glycerol or rather from allyl iodide made from glycerol. At the end of this long synthesis, therefore, the chemist is exactly on the spot whence he started. Friedel and Silva<sup>3</sup>, however, made glycerol in a different way. Trichlorhydrine is prepared from propylene chloride and saponified by heating with water. The propylene used is made from acetone. Wagner<sup>4</sup> produced glycerol by oxidizing allyl alcohol with potassium permanganate.

<sup>1</sup> *Ber d. chem. Ges.*, 1891, 24, 1007.

<sup>2</sup> *Ann. Chem.* (Liebig), 102, 339.

<sup>3</sup> *Bull. Soc. Chim.*, 20, 98.

<sup>4</sup> *Ber d. chem. Ges.*, 21, 3351.

Glycerol has also been formed synthetically by other investigators, but the principles involved are not greatly different from those set forth.

The first notice I have seen of the artificial formation of a fat is in a paper by Pelouze and Gelis<sup>1</sup> published in 1844. It is said that by gently heating a mixture of glycerol, butyric acid, and strong sulphuric acid, and afterwards diluting with water a yellowish oil separates. This fat is not soluble, or only slightly so, in water. It is soluble in all proportions in strong alcohol and in ether. Caustic potash breaks it up into butyric acid and glycerol. It may be formed at ordinary temperatures by passing a current of hydrochloric acid into a mixture of butyric acid and glycerol and afterwards diluting. The authors thought this body to be the butyrine discovered in butter by Chevreul. Its great solubility in alcohol would lead us in this day to suppose that the body was not a true butyrine.

Our present knowledge of the natural fats is based almost solely on the classic researches of Chevreul. While the work of Chevreul was purely analytic in its character, the knowledge of the constitution of fats which it disseminated has been the foundation on which all subsequent structures have been built. While at the present day chemists do not recognize the existence of margaric acid and margarine, all the other fatty bodies described by Chevreul have been found to have substantially the constitution which he assigned them.

Berthelot's first important contribution to the synthesis of fats was presented to the French Academy of Sciences on the 5th of September, 1853. It was entitled "Memoire sur les combinaisons de la glycerine avec les acides et sur la synthese des principes immediats des graisses des animaux."<sup>2</sup> From Berthelot's paper we learn that glycerol was discovered in 1779 by Scheele<sup>3</sup> in making lead plaster.

Fourcroy was the first to theorize on the nature of fats<sup>4</sup>.

Berthelot regarded the formation of soap as due to the affinity of oils for alkali.<sup>5</sup>

<sup>1</sup> *Ann. chim. phys.*, 1844, [3], 10, 434.

<sup>2</sup> *Ann. chim. phys.*, 1854, [3], 41, 216.

<sup>3</sup> *Opuscula*, 2, 175.

<sup>4</sup> *Système des connaissances chimiques*, 7, 142, 323, 329, and 334.

<sup>5</sup> Chevreul, *Ann. chim. phys.*, 88, 226.

Fourcroy in his work on the fat of cadavers, substituted another idea for this rational one, thinking the formation of soap due to the oxidation of the oil under the influence of alkali and air. He classed the vegetable oils, waxes, cadaveric fats, fats liberated from soaps by acid, cholesterine, etc., together under the name "adipocere."<sup>1</sup>

In 1815, simultaneously with the discoveries of Chevreul, Braconnot rejected the ideas of Fourcroy, saying :

"When tallow is agitated with acid or alkali, the three constituents, hydrogen, oxygen, and carbon, which had been in a state of equilibrium, separate and rearrange themselves in another order, giving rise to adipocere and to a very fusible fat, soluble in alcohol."<sup>2</sup>

Pelouze produced sulphoglyceric acids and phosphoglyceric acids and together with Gelis<sup>3</sup> he made butyrine, the first artificially prepared fat.

Berthelot has generalized this work by combining glycerol with both organic and inorganic acids. The bodies produced are, as a rule, neutral and incapable of directly uniting with alkali. Some reproduce the natural fats.

**Stearins.**—Stearic acid, melting at 70° and prepared according to the method of Chevreul,<sup>4</sup> forms with glycerol three neutral bodies, mono-, di-, and tristearin. The last is identical with natural stearin. To make monostearin; Berthelot heats equal parts of glycerol and stearic acid to 200° for thirty-six hours in a sealed tube. The body formed is insoluble in glycerol and readily separates from the excess of this body. It may be purified by heating to 100° with ether and quicklime to deprive it of excess of stearic acid.

To make distearin: This body may be formed by heating equal parts of glycerol and stearic acid to 100° for 114 hours, or to 275° for seven hours. It may also be formed by heating natural stearin to 200° for twenty-hours in the presence of glycerol. Another method is to heat monostearin to 260° for three

<sup>1</sup> *Ann. chim. phys.*, 3, 129; *Ibid.*, 5, 154; *Ibid.*, 8, 17, 23, 31, and 67.

<sup>2</sup> *Ann. chim. phys.*, 93, 271.

<sup>3</sup> Sur la acide sulfoglycerique, *Compt. rend.*, 21, 718; Sur la butyrine, *Nouvelles, Ann chim phys.*, 10, 455.

<sup>4</sup> *Recherches sur les corps gras*, page 206.

hours in the presence of three parts of stearic acid. However formed, it is to be purified by the treatment with ether and lime.

To make tristearin: This body is obtained by heating monostearin to  $270^{\circ}$  for three hours with fifteen or twenty times its weight of stearic acid. Water is eliminated. The product is to be purified with ether and lime. The properties of natural and artificial stearin coincide as nearly as can be expected, considering the fact that natural stearin is never obtained pure. The nearest approach in properties by natural stearin to those of the artificial, was that shown by a preparation made by P. Duffy<sup>1</sup> who purified it by thirty-two crystallizations. The acid prepared by saponification, etc., from the synthetic stearin had the same melting-point as that originally employed.

*Margarines.*—Margaric acid from human fat<sup>2</sup> forms two neutral combinations with glycerol, monomargarine, and trimargarine.

To make monomargarine: Monomargarine may be prepared by heating a mixture of glycerol and margaric acid to  $200^{\circ}$  for twenty-one hours or to  $100^{\circ}$  for 106 hours. The reaction takes place with great readiness, in fact the synthesis is easier than that of any other fat. The same body or a similar one, is formed by simple contact of the constituents at ordinary temperatures for three months, though in very small quantity. A margarine is also formed by heating a mixture of margaric acid and glycerol saturated with hydrochloric acid, to  $100^{\circ}$  for some hours, but it is always contaminated with chlorhydrine.

Trimargarine is formed by heating monomargarine to  $270^{\circ}$  for seven hours in the presence of excess of margaric acid. The fat acid separated from it by saponification, etc., had the same melting-point as that originally employed.

*Palmitins.*—Three palmitins were formed in the way employed for the preceding fats.

*Oleins.*—Three were formed. The oleic acid employed was purified by the method suggested by Gottlieb.<sup>3</sup> The commercial acid was twice chilled and filtered and then converted into a potash soap. The soap was dissolved in twice its weight of alco-

<sup>1</sup> *Quart. Jour. Chem. Soc.*, Jan., 1853, pages 303, 309, 310.

<sup>2</sup> Chevreul, *Recherches, sur les corps gras*, page 59.

<sup>3</sup> *Ann. der Chem. u. Pharm.*, 37, 93.

hol, filtered cold, and precipitated with barium chloride. The barium soap was recrystallized from boiling alcohol (one liter of strong alcohol dissolves five grams), and then decomposed by tartaric acid in an atmosphere of hydrogen.

Valerines, butyrines and acetines were formed in the same general manner.

All these fats could also be produced, and more easily, by heating the components to  $100^{\circ}$  in the presence of an auxiliary acid, such as sulphuric, hydrochloric, tartaric, phosphoric, etc. Triacetine has also been formed by Böttenger<sup>1</sup> by the action of acetic anhydride on glycerol in the presence of acid potassium sulphate.

In this direction the work of molecule building has been carried a step further in securing the construction of a higher glyceride containing phosphorus. Hundeshagen<sup>2</sup> has succeeded in preparing a substance similar to lecithin, which is one of the essential constituents of cell plasma. In this work he followed first in the steps of Berthelot in securing distearin (distearyl glycerol) by heating stearic acid with an equal volume of anhydrous glycerol for thirty hours in closed tubes at  $200^{\circ}$ . The purified distearin, heated to  $110^{\circ}$  with metaphosphoric acid or phosphoric anhydride, gave the desired phosphorus compound. Numbers of the salts and derivatives of the distearyl glycerol phosphoric acid have also been prepared and studied.

In the matter of sugars greater progress has been made. The elder Thenard, more than fifty years ago, proposed a scheme for the direct production of sucrose by the condensation of carbon dioxide, water, and ethylene. Kiliani, Tollens, and many others have made important contributions to this work, but by far the most important advances in the synthesis of sugars have been made by Fischer. His work has been most thoroughly reviewed in this country by Keiser<sup>3</sup> and Stone.<sup>4</sup> Fischer<sup>5</sup> has also published a résumé of his work. Starting with formaldehyde and passing through glycerol and acrolein, Fischer, by a series of beautifully conceived researches, has succeeded in forming,

<sup>1</sup> *Ann. Chem.*, 263, 359.

<sup>2</sup> *J. prakt. Chem.*, neue Folge, 28, 219.

<sup>3</sup> *Am. Chem. J.*, 11, 277, and 12, 357.

<sup>4</sup> *Ag. Science*, 6, 166.

<sup>5</sup> *Ber d. chem. Ges.*, 23, 2114, and 27, 3189.

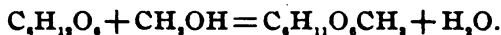
by synthesis, a large number of sugars, some of which have not been discovered in nature. For the details of this work, the reviews mentioned can be consulted.

Lately in the same direction, another step has been taken. Fischer and Bunsch<sup>1</sup> have shown that the sugars under the influence of hydrochloric acid in the presence of alcohols and oxyacids are condensed to polysaccharides resembling glucosides.<sup>2</sup> Of these bodies methyl glucoside,  $C_6H_{12}O_6 \cdot CH_3$ , methyl arabinoside,  $C_6H_{12}O_6 \cdot CH_3$ , ethylarabinoside,  $C_6H_{12}O_6 \cdot C_2H_5$ , ethylglucoside,  $C_6H_{12}O_6 \cdot C_2H_5$ , methylgalactoside,  $C_6H_{12}O_6 \cdot CH_3$ , ethylgalactoside,  $C_6H_{12}O_6 \cdot C_2H_5$ , and benzylarabinoside,  $C_6H_{12}O_6 \cdot CH_2 \cdot C_6H_5$ , have already been formed.

Previous to the appearance of the above papers, Michael<sup>3</sup> had described a method for the synthesis of a glucoside. This method depends on the interaction taking place between so-called acetochlorhydrate and the alkaline carbolates. The method yields only a moderate product and is somewhat troublesome.

The process employed by Fischer in converting sugars into glucosidal bodies is well illustrated by the following example:

Grape sugar is dissolved in methyl alcohol and in the cold the solution is saturated with gaseous hydrochloric acid. The solution soon loses its power to reduce alkaline copper under this treatment and a crystalline product is formed. The reaction which takes place is represented by the following formula:



To this substance the name methyl glucoside is given. The other bodies named above are formed by similar reactions.

Fischer, however, freely admits that although synthesis has done so much in the way of producing compounds which heretofore have been deemed the exclusive product of living vegetable cells, yet in the case of sugars an essential difference still exists.<sup>4</sup> In the laboratory there is produced at first only an inactive sugar which afterwards, by means of special operations, is split up into the active modifications, while the assimilation

<sup>1</sup> *Ber. d. chem. Ges.*, 27, 2478.

<sup>2</sup> *Ber. d. chem. Ges.*, 26, 2400.

<sup>3</sup> *Compt. rend.*, 89, 355.

<sup>4</sup> Oration before the Institute for Military Surgeons, August 2, 1894, *Neue Zeitschrift für Rübensucker-Industrie*, 23, 185.



process of plants gives directly the active sugars of the same geometrical series. The stereochemistry of the carbohydrates, however, furnishes for this fact a full explanation.

If, in the case of an active sugar, by means of hydrocyanic acid, an additional carbon atom is added, the artificial process takes place in an asymmetric way. Since now in plant assimilation the optically active constituents of the chlorophyll granule take part in the production of carbohydrates, it is easy to understand how from the beginning, the formation of sugars with six carbon atoms takes place in an asymmetric manner.

In so far as I have been able to determine, no experiments have been made to determine the digestive coefficient of these synthetic foods. In the case of the artificial sugars many of them are unaffected by alcoholic ferments and it is safe to assume that the digestive ferments would be equally powerless to disintegrate them. The direct products of sugar synthesis are, as a rule, neutral to polarized light. This does not imply that morphologically they are so different from the natural products, but rather that the carbon asymmetry is inversely twinned and the product is composed of equal quantities of right and left-handed sugars.

Of the natural sugars, levulose is the only left-handed one of any economic or digestive importance. The specific rotatory power of this body varies with the temperature, and at 88° the disjointed carbon atoms are so much reduced in position as to show a rotatory power equal to that of dextrose.

So far, it does not appear that the left-handed sugars made by synthesis have all the properties of levulose. They seem to be somewhat different in their stereometric relations from the natural product. In fact, the theory does not require that the left-handed sugars be levulose, but that they be simply the twin asymmetric duplicates of the right-handed varieties. Left-handed dextrose, therefore, is an entirely different substance from levulose. For the old name dextrose, Fischer uses glucose, and for levulose, fructose. The prefixes l., d., and i., signify left and right polarizing and inactive respectively. In one case, however, he has discovered a. d. fructose as well as a. l. glucose.

We have seen how by slow and painful steps and by round-

about ways the synthesis of sugar has gradually progressed until products containing nine molecules of carbon have been obtained. The ordinary sugar of commerce, saccharose, contains a molecule with twelve atoms of carbon. This sugar, however, can not be strictly considered as a dodekose, for it appears to be the product of the condensation of two hexoses. Whatever may be the true theory of its composition, whether wholly of the aldehyde type or a hybrid aldehyde ketone, yet its structure is of a higher order than the simple hexoses and it has not been formed artificially by any of the usual processes of synthesis.

It has remained for an inventor to take a short cut across the synthetic field and make saccharose *per saltum*.

Jean Ercole Pelligrini, a citizen of Italy, residing in France, has taken out a patent in this country for making sugar in a thoroughly direct manner. Ethylene gas, carbon dioxide, and steam are admitted in proper proportions to a channeled cube of pumice stone, impregnated with platinum sponge. The carbon dioxide and ethylene are used in practically equal volumes and the steam *ad libitum*. The pressure is so regulated that each gas will gradually diffuse through the whole porous platinized space. The operation is continued for about half an hour and "at the end of this period" to quote the language of the letters patent, "a sirup containing from twenty to twenty-five per cent. of sugar is withdrawn."

A sample of the sirup submitted with the application for the patent was examined in the laboratory of the Division of Chemistry at Washington and found to be sucrose. That it was made in the manner described, however, is a matter which, to my mind, requires further demonstration. The examiners of the Patent Office were, nevertheless, assured of the genuineness of the sample, by what proof I know not. For my part, I do not believe that a single molecule of sucrose can be made by that process. Some simple organic acid might be produced in this way, possibly some inactive sugar, but where shall we look for the stereochemical asymmetry which is so predominant a feature in that complex molecule which we call saccharose?

But for the sake of argument, grant the actual production of this substance. The price of a pound of carbon dioxide is far

greater than that of a pound of sugar, and ethylene is still far more expensive. If the process of Pelligrini really works as well as the United States has certified, the sugar would cost nearly a dollar a pound. The whole process, in my opinion, may be classed with the electrical refining methods so successfully employed a few years ago in scientific buncoing. A full exposition of the fallacies of the method is given by Maumené.<sup>1</sup>

In the foregoing pages I have attempted to give a synopsis of some of the forms of organic synthesis which would enable us to come to a definite opinion regarding the possible production of artificial food. The prospect, it must be admitted, is not a flattering one.

First of all, it is seen that all cases of successful synthesis from an economic sense, belong either to the class already mentioned, *viz.*, retrograde synthesis, or to a process depending on the use of already existing organic compounds.

In this direction chemistry has a wealth of future achievements to offer commerce. The changes and modifications which can be made in natural products will continue hereafter, as in the past, to present to chemical science problems of the most promising success. As in the case of the polysaccharide starch, from which a simple hexose sugar is produced of the widest use in the arts, so with other organic products of the field, many victories in retrograde synthesis may be won. Chemistry will show how to make many foods more useful, and in the way of cooking more nutritious and palatable. In respect of the direct or indirect union of the elements into successful food products, there is not a single instance in all that have been cited to give any hope whatever.

In the way of economy the simple synthesis of hydrogen and nitrogen to form ammonia has never seen any chance of economic success. Here in one way, at least, synthesis might help to increase the stores of food. Nitrogen in ammonia salts is now worth eighteen cents a pound to the farmer. A simple synthesis would materially reduce its price. It might be well for the ambitious chemist to begin with ammonia before attempting albumen. While the scientific difficulties are less formidable

<sup>1</sup> *Jour. de Fab. de Sucre*, 35, No. 4.

than the economic ones, yet they are apparently unsurmountable. A single pound of synthetic sugar must be worth many dollars, and we do not know that it will submit itself to digestion. The complex molecules of albuminoids and starches seem to me to be beyond the reach of chemical handicraft. There is no possibility of making many of the nutritive constituents of porter-house steak, much less the mixing of them into an attractive and tempting form. In the field of scientific research, however, and the light which will be thrown on molecular structure, there are no limits to the triumphs of synthetic chemistry.

As the periodic law among the elements, so the theories of stereostructure, isomerism, asymmetry, and condensation have led and will lead to the greatest discoveries. When the investigator is once convinced of the possibility of any compound he will never cease to look for it until its discovery crowns his efforts. As the disturbance caused by an unknown body in space leads the astronomer to train his glass on the unexplored depths of the heavens, so do the missing links in molecular structures incite the chemist to renewed exertions. This fact is beautifully illustrated in the case of the carbohydrates. In the last few years there have been added to the number of sugars known to be produced by nature, more than twenty built by synthesis. But large numbers of possible sugars are still missing.

According to Fischer,<sup>1</sup> every asymmetric carbon atom in a carbohydrate molecule makes two forms possible. There can, therefore, be at least eight hexoses, and each of these is optically paired, making sixteen in all. Ten years ago only two of like structure of this number were known. Now ten have been discovered, and six yet remain unknown. Of the pentoses there are eight possible forms, of which four have been discovered. Of the thirty-two possible heptoses, only six are known, and of the 128 nonoses, only two. Since the possible number of compounds increases in a geometrical ratio with the addition of carbon atoms, it is seen that the field for discovery is not soon likely to be exhausted. But the molecule builder, it seems certain, must take his stones from Nature's quarries. He may fashion and change them, adapt them to new uses and endow them with more

<sup>1</sup> Neue Zeitschrift für Rübenzucker-Industrie, 23, 169.

valuable properties, but he can not make them of the raw original materials.

Schorlemmer in the revised edition of his *Development of Organic Chemistry*, while taking a very sanguine view of the future progress of synthetic chemistry, does not expect it to interfere with the farmer. He expects, at most, morphia and quinia to come from the laboratory instead of from the poppy and cinchona.

Roscoe says: "But now the question may be put, is any limit set to this synthetic power of the chemist? Although the danger of dogmatism, as to the progress of science, has already been shown in too many instances, yet one can not help feeling that the barrier which exists between the organized and unorganized world is one which the chemist at present sees no chance of breaking down.

It is true that there are those who profess to foresee the day when the chemist by a succession of constructive efforts, may pass beyond albumen and gather the elements of lifeless matter into a living structure. Whatever may be said regarding this from other standpoints the chemist can only say that at present no such problem lies within his province. Protoplasm with which the simplest manifestations of life are associated is not a compound but a structure built up of compounds. The chemist may successfully synthesize any of its component molecules, but he has no more reason to expect the synthetic production of the structure than to imagine that the synthesis of gallic acid leads to the artificial production of nutgalls."<sup>1</sup>

It seems strange, therefore, that one of the most eminent of living chemists should have so unequivocally committed himself to the doctrine of future synthetic foods.

In an address before the Society of Chemical and Mechanical Industries in Paris, on the 5th of April, 1894, Berthelot publicly proclaimed his theory of the coming suppression of agriculture and the substitution of synthetic foods for its products. This theory he has more fully elaborated in McClure's Magazine for September 1894. The accomplishments in synthetic chemistry on which he bases his predictions are essentially those which

<sup>1</sup> Presidential Address, British Association, *Chem. News*, Sept. 2, 1887, p. 100.

have been set forth already in this address. With proverbial European provincialism, however; he fails to mention one of the strongest of the arguments he might have used; *viz.*, Fischer's sugar synthesis. The wildcat process lately patented in this country, however, as well as in France, for making sugar by the condensation of ethylene receives favorable mention and no doubt is entertained of the speedy manufacture of sugar on the largest scale synthetically and that the culture of the sugar-beet and sugar-cane will be abandoned because they will have ceased to pay. The struggling sugar planters of our own country who during the present season have been making sugar at a cost of four cents a pound and selling it for three, will bear witness to the fact that this happy period has already arrived.

The synthesis of the dyestuffs, especially of alizarin and indigo, he cites as examples of the destruction of an agricultural industry by chemical achievements. He dwells and very properly, on his own work in the synthesis of fats as evidence of what may be accomplished in that line. The beefsteak of the future may not be identical with that of to-day, but it will be a tablet of any color or shape desired and will entirely satisfy the epicurean senses of the year 2000. Chemistry has developed the whole science of cookery and flavoring and provided all the utensils of the kitchen. It remains now only for it to complete its work and furnish the food itself. Even at the present time, according to Berthelot, tea and coffee could be made artificially if the necessity should arise. The caffeine of the chemist has the following genealogy:

Carbon and oxygen beget carbon dioxide.

Carbon dioxide and chlorine beget carbonyl chloride.

Carbonyl chloride and ammonia beget urea.

From urea comes uric acid.

From uric acid is derived xanthin.

Xanthin yields theobromine.

Theobromine yields theine or caffeine.

From this pedigree it is concluded that tea plants, and cocoa and coffee trees will soon follow the madder and indigo plants into economic eclipse. No attempt is made to compute the cost of the caffeine necessary for a single cup of Java; and the fact that caffeine is only one of its constituents is naively ignored.

Tobacco also is soon to follow because something resembling nicotine has already been made synthetically. While nicotine has not yet been made synthetically, its near relationship to conine, the active principle of hemlock, which has been so formed, leaves little doubt of the speedy accomplishment of this desirable end.

In regard to the synthesis of food products directly from the elements attention is called to the following points :

By means of the electric spark acting on hydrogen and carbon at a white heat, acetylene is produced.

Acetylene will combine with another atom of nascent hydrogen forming ethylene and marsh-gas.

Ethylene can be made to combine with the elements of water forming common alcohol, while marsh-gas in similar circumstances, yields methyl alcohol.

Acetylene with nascent oxygen forms oxalic acid.

Acetylene in contact with nitrogen subjected to the electric spark forms hydrocyanic acid.

Acetylene and oxygen in the presence of water and an alkali form an acetate, whence acetic acid.

"I also found," says Berthelot, "that ethylene under certain conditions could be transformed directly into benzene. Here then we have seven familiar compounds of wide utility; acetylene, marsh-gas, alcohol, oxalic acid, acetic acid, cyanhydric acid, and benzene, to say nothing of many others which I might mention obtained from these elements direct. Now imagine for a moment the enormous number of organic compounds into the constitution of which, according to regularly acting laws, these seven different compounds enter. There are six different families of alcohols alone and each one of these families embraces a greater or less number of special alcohols. Over the whole field of organic chemistry the mystery of possibilities extends. Its combinations and intercombinations are so limitless that we can only work on regularly to ends that it is impossible to foresee."

According to Berthelot, the fields which are now defaced by agriculture will be beautified by regaining their natural covering and the earth will be one vast park of pleasure and the chemist the great conservator of the human race.

A synthetic climate will replace the capricious one furnished by nature. Winds and waterfalls will provide power and light, and the bowels of the earth, tapped by frequent wells to a great depth, will supply the superheated steam to turn the winter into spring and to bring together the pole and the equator. When these predictions are read we first think that Bellamy has turned chemist, and by reincarnation in the shape of the great Parisian Savant has thrust upon the scientific world a new edition of "Looking Backwards."

In all the instances brought forth there is not the slightest approach to anything to justify the prophecy of a period of artificial food. The few cases of synthesis in which the products approach the composition of anything digestible present such insurmountable difficulties in expense and supervision as to render any expectation of reaching economic results utterly futile. In the great majority of cases, as has been seen, the process of synthesis is conducted on materials already organized by living cells. The enormous cost of building up any kind of a commercial, synthetic organic body directly from the elements is such as to render it, in my opinion, utterly improbable of successful achievement.

Even if food products can be formed in the crucible there is no reason whatever for supposing that they can ever play any rôle in an economic sense. The untold billions of laboratories which nature builds are infinitely cheaper in construction and operation than those filled with platinum and porcelain. The sun ignites the crucibles of nature at an expense far less than attends the use of the city gas works. The director of Nature's laboratory depends on no endowment nor legislation for his salary and his bills for supplies are not disallowed by any board of auditors on the score of economy. Night and day his patient faithful assistants work without thirst for fame, without hope of reward. They fight not for priority of discovery and their anonymous papers are printed in rich profusion in the great *Berichte* of the universe. The chemistry of the chlorophyll cell is far more wonderful than any of the achievements of Lavoisier, Berzelius, or Fischer.

It would doubtless be a solace to the weary toiler in the sun to



look forward to a time when he might lie in the shade while proteids were pricking up their ears in the condenser and fats frying in the scientific pan. But in the days of the far future, while Berthelot will still be honored and Fischer praised, the farmer will be found following in the furrow, fields of waving grain will brighten the landscape, and herds of kine graze upon the hills.

*Members of the Society:*

According to the provisions of our Constitution, the time has arrived when I am to take my leave of you as President of the Society. I thank you most heartily for the honor twice conferred upon me of presiding over this great organization. It is only fitting at this moment that I should give a brief account of my stewardship.

One of the most gratifying features in connection with the history of the Society during the past two years, is the increase in membership. In two years, according to the data furnished by the Secretary, the Society has more than doubled its membership. Our membership now is well up to the thousand mark. I should have been better pleased at this time to take leave of a membership of fully 1,000, but I feel sure that this number will soon be reached.

The JOURNAL of the Society has fully kept pace with the increase of membership. The volume for 1893 contains 720 pages, devoted almost exclusively to original articles, of which 98 appeared. The volume for 1894 contains 891 pages, exclusive of proceedings, and 158 original articles. In addition to the copies furnished the members of the Society, there is a large number of subscribers to the journal in this and foreign countries, so that the total circulation at the present time is over 1,000. It is recognized as a leading chemical journal by the editors of foreign periodicals. More than thirty of its articles, during the past year, have been reprinted wholly or in part in the *Chemical News*, and a large number of abstracts has appeared in the *Journal of the English Society*, the *Berichte*, and the *Central-Blatt*, in which, during the past twelve months, over 100 abstracts of articles from the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY have appeared. These are figures which are very gratifying to us all.

The prosperity of the Society has been due to united action among all its members, and a determination to make it a success.

Local Sections have been established during the past two years in Washington, the Lehigh Valley, and in New Orleans. The chemists of the Pacific Slope have also expressed a desire to unite with the Society at an early date and establish a Local Section. There are many other places where the membership of the Society would justify the establishment of Local Sections, and especially is this true of Baltimore, Philadelphia, Boston, Cleveland, and Chicago, and it is hoped that speedy action may be taken to secure these desirable results.

To the editor and the Committee on Publications the Society is indebted for energetic and systematic work in increasing the efficiency of the JOURNAL, but the efforts which these gentlemen have made would have had but little success had not the members of the Society throughout all parts of the country come forward with contributions of papers. There are often good reasons why a paper on any particular subject should be published in a particular journal in this or other countries, but as a rule it seems to me that American authors should first offer their papers to American journals, and if this rule is followed it is certain that the journal of our own Society will receive a fair share of the contributions. We would not desire to exclude from the field any other journal, but we are justified in asking that due consideration be given our own journal by our members in the distribution of their papers.

The American Chemical Society represents American chemical science as a whole and therefore it is desirable that the journal of the Society should not become the organ of any particular branch of chemical science. The editor and the Committee on Publications have kept this end in view in the distribution of the articles and have endeavored to put into each number something of interest to many of the special departments of chemical science. Our doors are open for the entrance of those engaged in didactic chemistry, for organic chemists, for technical chemists, for agricultural chemists, for mining and assaying chemists, for general manufacturing chemists, and in fact for every branch of our great science. The journal being thus cosmopolitan brings to every

chemist not only matter relating particularly to his branch of study, but also a general idea of what is going on in other fields of activity. He, therefore, who desires to keep abreast of the work of the times and avoid becoming narrow in his views and practices, can not find a better means to this end than membership in our Society. The American Chemical Society has no quarrel with any chemical sect or any institution of learning, but will endeavor to make itself useful to all. It would especially seek to foster a spirit of scientific patriotism in this country, a belief in American science and American scientists, and to diminish, to a certain extent, the blind worship of foreign institutions which, in some instances, has been so characteristic a feature of American workers. I would not say anything to discourage a young man from seeking a part of his education abroad, but I would certainly encourage foreign chemists to seek a part of their education in this country. It is not quite right for the United States to contribute so many students and so few professors. While the American student may find benefit from a course of study abroad, the foreign student would find equal benefit by a residence at some of the great institutions of learning in this country. If professors of chemistry desire to attract students from abroad they must recognize their own country in its scientific institutions. They can not afford to remain outside of the great organized body of American chemists and to send their contributions all to foreign journals if they wish their own institutions to grow in favor at home and abroad. While we are proud therefore, of our large membership, it is evident that for every one who is now a member there are at least two who should become so.

There are nearly 4000 men in the United States who are engaged directly in chemical pursuits, and it is not too much to ask that at least fifty per cent. of this number should become affiliated with the American Chemical Society. We will not consider that we have attained our normal growth if at the end of the next quinquennial period our membership shall not reach fully 2000. To this end let each of our members pledge his word and exert his influence and the work will be accomplished.

I can not close this address without expressing my thanks to

the Secretary of the Society for the efficient method in which he has conducted the work of his office, arduous and exacting as it has been, and to the Directors and Councilors of the Society for the support which they have given me in all matters connected with the executive conduct of the presidential office.

In the little which I myself have been able to do, I have had in view only one object; *viz.*, the welfare and prosperity of the Society. It may be that in some cases offence has been given to members of the Society by the manner in which my work has been done, but I am sure that those who have intimate knowledge of the motives which have actuated my conduct will bear witness to the fact that such offence was not given with malice or meaning.

To my successor I may say that he will find the officers, councilors, and directors, remaining as they do mostly unchanged, full of zeal in the work of building up the Society and ready at all times to support him in the conduct of his office.

---

## THE DETERMINATION OF PHOSPHORIC ACID.

BY H. PEMBERTON, JR.

Received January 27, 1895.

THE method of determining phosphoric acid by the alkali-metric titration of the yellow precipitate, has been employed, lately, by a number of chemists and has been made a subject of investigation by the Association of Official Agricultural Chemists. A report upon the subject has been embodied in its last bulletin.

There are a few points regarding this method to which attention should be drawn.

In preparing the standard alkali its strength is, of course, established by testing it against acid of known strength. In doing this, it is important that the indicator used should be phenolphthalein, and *not* methylorange. Potassium hydroxide almost invariably contains alumina, and such a solution gives the neutral reaction with methyl orange *before* it gives it with phenolphthalein. Consequently if methyl orange is used in the standardizing and phenolphthalein is used in the titration of the

yellow precipitate, too much of the alkali will be used in the latter case, and the results will be high.

The same reasoning holds true in case a little carbon dioxide is present in the alkali.

In regard to the precipitation of the phosphoric acid by the aqueous solution of the molybdate, the following directions were given: Heat is now applied, and the solution brought to a full boil. It is then removed from the lamp, *no more heat being applied*. (This JOURNAL, 15, 387.)

I have italicized here in order to draw attention to this point. If the volume of the phosphate solution is from fifty to seventy-five cc., it will be found, after adding five cc. of the molybdate, say three times (fifteen cc. in all) that the temperature of the solution will be about 70° C., which is about the proper temperature for the precipitation. In other words, the solution, once heated, will take care of itself, (if I may use the expression) and does not require a water-bath of definite temperature, or any testings with the thermometer.

There is another point in connection with this precipitation that is of interest. It is well known that a precipitate that has a crystalline or coarse structure is more easily washed, and is less liable to carry down impurities, than a precipitate obtained in a finely divided condition, or as a "mud." Thus in separating lime as sulphate, from iron and alumina, in Jones' process, the alcohol is not added until most of the calcium sulphate has crystallized out from the aqueous solution. Were the sulphuric acid added to the alcoholic solution the precipitate would certainly be impure. In like manner, in potassium determinations, we evaporate the solution nearly to dryness (although it takes this extra time), in order to obtain the platinum salt in a crystalline state. Again in precipitating phosphoric acid by magnesia mixture, the latter is added slowly, drop by drop, "stirring vigorously," in order to prevent contamination. In the same way, when precipitating by the aqueous molybdate, I am accustomed to run the contents of the five cc. pipette into the solution *not* in one continuous stream, but by interrupting the flow from the pipette by momentarily touching the end of the pipette with the finger, *stirring* the solution as it goes in. Thus

the precipitate does not come down *en bloc*, in presence of a great excess of molybdate, but forms in a solution that is comparatively bare of molybdenum until the precipitate is nearly all down. The washing of the precipitate is best conducted, with the use of a vacuum, on a Hirsch porcelain funnel, smallest size, or as described by Mr. B. W. Kilgore, on a porcelain disk, (the disk to be covered with filter paper) with rubber rim in three inch glass funnel. In either case, soft paper from cut filters is better than that bought in sheets. Others have used the Gooch crucible, with advantage. With the Hirsch funnel I find that a precipitate containing forty mgms. of phosphorus pentoxide is thoroughly washed by 300 cc. of water. I may say here that fifty mgms. of phosphorus pentoxide is about the largest quantity that it is well to work upon, when employing a suction-pump. Chemists who do not use suction had better employ not more than thirty to forty mgms. The phosphomolybdate is a difficult precipitate to wash, being like lead chromate in this respect.

The nitric acid, sp. gr. one and four-tenths, and the ammonium nitrate solution, are best kept in graduated glass cylinders of 200 to 300 cc. capacity, the mouths of which are kept covered by small beakers. The quantity desired to be poured out can then be read off on the graduation.

The molybdate solution (which should be neutral, and is best freed from any insoluble molybdic acid by filtration), can be kept in an ordinary narrow-mouth bottle. A wide, flat cork covers the mouth of this bottle, and through the center of this cork the stem of a five cc. volume pipette is held tight. This pipette rests, when not in use, in the molybdenum solution, and the cork prevents the entrance of dust. Mr. Kilgore has applied the ordinary nitric acid solution of the molybdate, to this volumetric process, with good results. He heats the solution on a water-bath having a constant temperature of 60° C. Mr. F. Bergami adds to his solution of the phosphate (containing already about three cc. of strong nitric acid), ten cc. of ammonia, sp. gr. 0.90, and then fifteen cc. of nitric acid, sp. gr. 1.40, and then, after heating to boiling, proceeds with the aqueous molybdate, in the usual way. Mr. L. A. Voorhees, precipitates with the nitric acid solution of the molyb-

date *in the cold*, allows to stand, at the temperature of the room, over night, and titrates in the morning. The details of these modifications are given in the 1894 report of the Association of Official Agricultural Chemists, published at Washington, D. C. Whatever modification may be used, the volumetric method will be found much quicker than the gravimetric, and, after a little experience, fully as reliable.

PHILADELPHIA, Pa.

## ON THE ESTIMATION OF SULPHUR IN PYRITES.<sup>1</sup>

BY G. LUNGE.

Received December 20, 1894.

UNDER the above title, Mr. T. S. Gladding (This JOURNAL, June, 1894), has published several modifications of the wet assay of pyrites which call for some comment on my part, since these modifications purport to be improvements on my method, contained in the "Alkali-makers' Handbook," and extensively employed in all countries.

Some of Gladding's modifications are of a less important character, and these can be passed in review very briefly. He does not, like myself, test the sample with its natural moisture, estimating the latter in a special sample, but he dries the whole sample and weighs it out in that state. He employs a whole gram of pyrites, I only half a gram; and I do so purposely, because the washing of the precipitates is much easier, and consequently the results are more reliable with the smaller than with the larger quantity. In lieu of the mixture of acids employed by me (three volumes of nitric acid of sp. gr. 1.42 and one volume of fuming hydrochloric acid) Gladding decomposes the pyrites with a solution of bromine and nitric acid. The prescription for that solution is not correct as printed, for seventy-five grams of potassium bromide can not possibly be dissolved in fifty grams of cold water, or anything like that quantity, but this may be a clerical error, which does not matter very much, as ultimately the solution is diluted to 500 cc. I will say at once that the bromine solution works well, but no better than the acid mixture according to my prescription.

<sup>1</sup> Read at the Boston Meeting, December 28, 1894.

A more important modification is the following: It is well known that in the presence of iron the precipitate formed by barium chloride in a solution of sulphates can not be freed from iron, and that the results of the estimation of sulphur in this case are too low; in my publication of 1879 (*Ztschr. anal. Chem.*, 19, 419) I found on the average 0.19 per cent. too little sulphur, unless the iron had been previously removed from the solution. Fresenius has also worked on this subject, and Jannasch and Richards, in 1889, completely elucidated it by proving that a double sulphate of barium and iron was formed in this case. Gladding gives a similar explanation, without mentioning the more complete investigations of his predecessors, which would have saved him the trouble of working out the matter for himself. I had already long ago dealt with that difficulty by proposing, in 1889, that method which was afterwards embodied in the "Alkali-makers' Handbook," *viz.*, precipitating the iron by ammonia, washing the ferric hydroxide, and precipitating the sulphate in the filtrate by barium chloride. Gladding asserts, however, that "the most careful washing failed to wash out all the sulphur from the ferric hydroxide," and he therefore proposes to wash the hydroxide as well as possible and to dissolve it afterwards in diluted hydrochloric acid, thereupon treating that solution with barium chloride; evidently with the tacit assumption that the small quantity of sulphide present in that solution is accurately enough estimated as barium sulphate, in spite of the large quantity of iron present; but that assumption is far from self-evident, nor does it actually represent the truth, as we shall see.

It is quite evident that Gladding, although he knows and quotes the "Alkali-makers' Handbook," and although he entirely adopts the prescription given there (page 93) for the *precipitation* of the ferric hydroxide, which deviates not unessentially from those previously given by Fresenius and others, has not completely followed the instructions for the *washing* of the precipitate given immediately after in the following words: "Filter hot, and wash on the filter with hot water, avoiding channels in the mass, but so that the whole precipitate is thoroughly *churned up* with the water each time." Many hundreds of pyrites tests made in my own and other laboratories have



proved that by following the above instructions the washing of the ferric hydroxide is accomplished in from half an hour to an hour, that the number of washings need not exceed five, and the bulk of the liquid, apart from the original filtrate, need not exceed 100 to 150 cc., and *that no trace of sulphur is left in the ferric hydroxide*, as evidenced by drying the precipitate, fluxing it with pure soda, dissolving it in water, and testing the solution for sulphate. It is true that the students in my laboratory have sometimes failed to get out all the sulphur, but in *every* case through having washed in the usual way, instead of that described above; and the same men have succeeded in *every* case, after their attention had been drawn to this point.

There is another difference between Gladding's and my own manner of proceeding. I prescribe heating the solution of the sulphate to the boiling-point, as well as that of the barium chloride, adding the latter to the former all at once, allowing to stand for half an hour only, and then at once filtering and washing while the liquid is quite hot. I had convinced myself that under these circumstances the precipitate filters most easily, and no barium sulphate whatever subsequently separates from the filtrate. Gladding, however, not merely adheres to the old and useless prescription of letting the liquid stand over night after the precipitation, but he adds to this a novel and most tedious way of effecting the precipitation, *vis.*, adding fifty cc. of barium chloride solution quite slowly, one drop per minute. This will take about an hour, instead of a few seconds, as in my method.

I considered it my duty to find out whether the method recommended by Gladding is better than mine, or inferior to it, or equivalent with it; and in the last case, which of the two is easier and quicker to execute. For this purpose a sample of Spanish pyrites was selected which was triturated as usual and mixed in the most careful manner. The tests were made by one of my demonstrators, H. von Keler, under my constant personal supervision. First of all the sample was tested exactly according to the method laid down in the "Handbook," with the following results: 50.17; 50.42; 50.20; 50.23; 50.19; average, 50.24 per cent. The insoluble amounted to 1.42 per cent; the moisture to 0.47 per cent. I abstain from reducing the percentages to the dry state, as being unnecessary in this case.

As the next step, a number of samples were decomposed by Gladding's mixture of bromine solution and nitric acid. We found his prescription in this item to be perfectly correct; it is not feasible to hasten the process (which is much lengthier than that used by myself), for instance, by filling the water-bath from the first with hot water. Any attempt to do such a thing ends in an over-violent reaction, and a loss by spurting and separation of free sulphur. We tested, of course, our bromine and potassium bromide, and found them quite free from sulphuric acid.

Three of the samples thus decomposed, according to Gladding, were precipitated exactly according to his method (one hour's precipitation, twelve hours' settling), another three samples according to mine (precipitating all at once and filtering after half an hour). The results were:

Gladding's Method.	Lunge's Method.
50.24	50.24
50.24	50.22
50.30	50.28
<hr/>	<hr/>
50.26	50.25

We see that both methods of precipitation give identical results, and these also entirely agree with the tests made from the first according to the "Handbook" method, *viz.*, 50.24. The conclusions to be drawn therefrom are: 1. Since both methods of precipitation yield the same result, my expeditious method of precipitation and filtration, which, inclusive of washing, takes about an hour, is preferable to Gladding's method, requiring about twelve hours. 2. Since Gladding's bromine method for decomposing pyrites yields results identical with that prescribed by myself, there is no reason for abandoning the latter and adopting a more tedious method, unnecessarily employing such a disagreeable reagent as bromine.

I understand from a private communication of Mr. Gladding's that he attributes the greatest value to his manner of precipitating the barium sulphate, and that in his opinion by operating in my way barium chloride is always carried down with the sulphate, making the results too high by 0.20 to 0.40 per cent. It would have been most remarkable if that point had been over-

looked in the many thousands of tests made according to my methods by perhaps a hundred different chemists; but in order not to incur any reproach, I had this point put to another searching investigation. Mr. W. Jackson made five most careful tests of another sample of pyrites, decomposing and otherwise treating them absolutely in the same way, but making the precipitation in two cases by Gladding's, and in three cases by my method. The results were :

Lunge's Method.	Gladding's Method.
50.59 per cent.	50.60 per cent.
50.63 " "	50.66 " "
50.56 " "	....

Average, 50.59 " "

Average, 50.63 " "

This affords another thorough refutation of Gladding's assertion.

In all analyses made up to this point the ferric hydroxide had been precipitated and washed five times, exactly in the way described by me; in every case it had been afterwards tested by fluxing with soda, but no trace of sulphur had ever been found. This furnished an additional (although unnecessary) proof that Gladding's assertion in that respect is equally unfounded, and that the treatment described by him (dissolving the ferric hydroxide in hydrochloric acid and precipitating by barium chloride) is quite useless, when observing the precautions in washing, pointed out by me. Still I thought it advisable to find out how Gladding's process would work in cases where, by some mistake, a little sulphur had been left in the hydroxide, and I grant that in important cases the latter ought to be tested in some way or another for any sulphur left behind. I further grant at once that in this case Gladding's method, as described, is more expeditious than mine: drying the ferric hydroxide, detaching it from the paper, mixing it with pure sodium carbonate, fluxing it in a platinum crucible (in such manner that no sulphur from the gas can get into the mass, *e. g.*, in a hole made in asbestos cardboard), dissolving in water and precipitating the sulphur by barium chloride. It is hardly necessary to say that I did not choose this plan without first considering the very simple method described by Mr. Gladding; but I rejected

it, since Fresenius had proved that barium sulphate is very distinctly soluble in an acid solution of ferric chloride. But as Gladding now asserts that the direct solution of the ferric hydroxide in hydrochloric acid yields accurate results, it became incumbent upon me to examine this statement.

Eight samples of our pyrites were decomposed, and the ferric hydroxide was precipitated under absolutely equal conditions of dilution, temperature, and quantities of reagents. The washing was purposely not continued as far as it ought to have been; and as some previous experiments had shown that no uniform degree of exhaustion can be attained by incomplete washing, we estimated in all cases the *total* sulphur, separating, of course, that which was found in the filtrate and that which was left with the ferric hydroxide. Four of the eight samples were treated by Gladding's prescription, and four by my own system. The results were :

Lunge (fluxing with sodium carbonate).			Gladding (dissolving in hydrochloric acid)		
Filtrate.	Precipitate.	Total.	Filtrate.	Precipitate.	Total.
49.64	0.60	50.24	48.98	1.03	50.01
49.36	1.01	50.37	48.84	1.39	50.23
49.07	1.21	50.28	49.02	1.07	50.19
49.25	1.04	50.29	49.30	0.73	50.03
Average,		50.29	Average,		50.09

This proves that Gladding's method does not, in this particular, give accurate, but *low* results (by 0.20 per cent.) ; with less complete washing the discrepancy would evidently have been even greater. The total sulphur found by my process, on the other hand, agrees quite satisfactorily with the correct analyses quoted before.

The final conclusion of this investigation must be: That in most points Gladding's method is correct, but in *not a single case* more so than my method; his modifications can not be approved, as they greatly lengthen the time required for the analysis, without any corresponding advantage whatever. In one point which forms the principal novelty in Gladding's process, he is decidedly *wrong*. It is not true that it is unavoidable to leave any sulphur in the ferric hydroxide; on the contrary this is very easy to avoid. If it has, after all, happened by incorrect manip-

ulation, Gladding's plan will *not* get out all the sulphur, but my plan (fluxing with soda) must be adopted.

I have shown that there is not a single point recommended by Gladding, in deviation from my method, which is fit for adoption, and I must conscientiously advise my brother chemists to adhere to the method just as I have laid it down in the "Alkali-makers' Handbook."

In conclusion I would add that I have also tried the method recommended by F. Johnson (*Chem. News*, 1894, 70, 212), omitting to precipitate the iron, but reducing it by sodium hypophosphite to the state of protochloride. Even when working precisely as described by the author, the results were so widely off the truth, that I can make nothing whatever of this plan.

## IMPROVEMENT IN THE MANUFACTURE OF ACETONE.<sup>1</sup>

BY E. R. SQUIBB, M.D.

Received January 17, 1895.

THE increasing use of acetone as a chemical solvent, and especially the relation of acetone to the manufacture of chloroform, gives importance to any improvement in its production.

Up to this time the writer knows of no process of manufacture except by the destructive distillation of acetates at high temperature. The acetates are charged into stills and heated as long as they yield any acetone. Then the acetates being decomposed to waste carbonates are discharged and the stills recharged with fresh acetate, making an interrupted process of repeated charging and discharging and heating and cooling. This process is very old; but two patents have been taken out in this country on some details of the process and apparatus.

The writer proposed to himself to make acetone directly from acetic acid by a continuous process, and has accomplished that object.

In Gmelin's Handbook of Chemistry, Cavendish Society edition, 1853, 8, 291, under the head of decomposition of acetic acid by heat, much work is given where the vapor of acetic acid was

<sup>1</sup> Read before the N. Y. Section, January 11, 1895.

passed through heated tubes, acetone being one of the products; and, on this line of investigation, the writer's work was taken up.

It was not difficult to see that the discrepant results reached by the authorities were due to differing physical conditions, and different degrees of heating, since it was mechanically quite certain that a current of vapor passing through a stationary tube, heated from below, whether empty or filled, could not be heated to the same degree in all parts of the tube, and therefore could not give the same decomposition in all parts.

The work undertaken was commenced in very long-necked glass bulbs, held in a horizontal position, so that they might be stationary or be revolved by hand, and these were heated by a bath of Wood's metal—the acid being passed in, and the products coming out through horizontal tubes in the long necks.

Experiences with these bulbs led to much better mechanical devices. A small flask was arranged as a still, and from this, by a gas-burner, a constant current of acetic acid vapor could be produced at any desired rate. The rate was regulated by the rate of supply of liquid acid from an elevated graduated supply vessel, the supply going to the still through a glass tube, in which the rate of dropping was seen and controlled by a stop-cock. Then, by varying the acid supply and the heat from the burner, the boiling liquid in the still could be kept at about a constant level, and with a controllable known rate of vapor supply.

At some distance from this end of this apparatus the condensing apparatus was arranged to receive the distillates. The products of distillation were first received in a flask where most of the watery vapor and undecomposed acid was condensed, but where the temperature continued so high that but a mere trace of acetone was arrested there. From the neck of this flask the remaining gases and vapors passed through a good condenser, which delivered the remainder of the water and undecomposed acid and the acetone into a flask immersed in an ice-bath. Here almost all the condensible vapors were condensed. The gases and uncondensed vapors were taken from the neck of this flask to a small wash-bottle supplied with water, by which the current of gases was washed. Here waste acetone enough was caught to increase the volume of contents to a point at which all went off

together in the current of gases, and the level remained constant. Next was a wash-bottle containing a strong solution of sodium hydroxide. Through this the residual gases were passed in order that most of the carbon dioxide might be combined. Finally, the gases were passed through another small wash-bottle containing water. At the small exit tube of this bottle the gases were tested for inflammability, and the proportion of methane and carbon monoxide was estimated by the absence or the degree of inflammability. Except at the times of testing, this exit tube was connected to a Sprengel water-pump, and a minus pressure of one to six cm. of mercury was maintained on the entire apparatus. This served to relieve all joints and connections and caused all the leakages to be inward, whilst a mercury-gauge at each end gave due notice of obstruction or irregularities.

These two ends of the apparatus remaining constant, the intervening space was occupied by the varying form of distilling or decomposing apparatus. An earthenware drain-pipe, with movable tile ends served as a furnace. This drain-pipe, supported in a horizontal position, had six holes drilled above and below. Each lower hole was large enough to admit a Bunsen burner with limited air space around it, while the holes on top, to give exit to the products of the combustion were smaller. The decomposing tubes or stills of wrought iron, with cast iron ends, occupied this drain-pipe furnace, being connected with the vapor supply apparatus at one end and the condenser at the other.

Much preliminary work was necessary in getting the apparatus in good working order, and in following up tangential points, but these are passed over, and only the important work given—and that not always in the order in which it was done, but in an order which brings the results into a more logical sequence more easily understood.

Two strengths of acetic acid were used. First, an acid containing thirty-six per cent. of absolute acid. But as this gave distillates unnecessarily dilute it was generally given up in favor of a sixty per cent. acid, although the reactions were not noticeably different in the use of the two strengths. Hence with two exceptions the results given are from a sixty per cent. acetic acid.

Reducing the work from the disorderly way in which it was done to a natural order, and rejecting what was not trustworthy, it is best to begin with some repetitions of work already long on record. (See Gmelin's Handbook, and other authorities.)

A tube of wrought iron about thirty-six cm. (fourteen inches) in length by six and five-tenths cm. (two and five-tenths inches) internal diameter, reduced at each end to tubing of about six-tenths cm. (one-fourth inch), was held stationary in the center of the furnace, and connected at one end with the acid vapor supply and at the other with the condensers. This tube could be heated by the gas-burners to any desired degree up to a dull red heat. The trials were made under as nearly the same conditions as practicable, the running time being about three and five-tenths hours, and under close observation. The amount of sixty per cent. acetic acid which could be passed in, in vapor during this time, varied much—generally 250 to 350 cc. The quantities used were always reduced to absolute acid ( $\text{HC}_2\text{H}_3\text{O}_2$ , = 59.86), and the results are given in the same acid, but a high degree of accuracy was impracticable, and therefore not aimed at.

(1) With the tube empty and heated nearly to redness at first, and finally to a dull red heat, 290 cc. of sixty per cent. acid = 174 grams absolute acid, was passed in in three and five-tenths hours. About 111 grams of this acid passed through unchanged, and sixty-three grams were decomposed. That is, about 63.8 per cent. came through unchanged, and 36.2 per cent. were decomposed. In the first receiving flask, kept hot by the vapor, there was no acetone, but only 132 cc. of a fifty-three per cent. acid. In the second flask, in the ice-bath, there was 115 cc. of a thirty-six per cent. acid; and this liquid, roughly estimated by the iodoform test, contained ten to twelve per cent. of acetone. From the final wash-bottle came a stream of inflammable gas—probably methane and carbon monoxide—that would burn almost continuously.

(2) Next, this stationary tube was filled with coarsely granulated pumice-stone, freed from large pieces and from dust, and so tightly packed as to have spring enough to keep the tube full when expanded by heating. Into this, in three and five-tenths



hours, 189 grams of absolute acid, in vapor, were passed, and yielded in the first, hot flask 103 cc. of fifty-four per cent. acid = 55.62 grams absolute acid. In the second, ice-bath flask 138 cc. of 38.4 per cent. acid = 52.97 grams of absolute acid, making 108.6 grams out of 189 grams distilled over unchanged, and 80.4 grams decomposed. The contents of this second flask were about 14.5 per cent. acetone. The stream of inflammable gases was estimated as being not less but rather greater than with the empty tube.

(3) Next, took the pumice from the tube, divided it into two parts, and rejecting one-half, intimately mixed with the other half 500 grams of dry, precipitated barium carbonate. Charged the tube with this mixture, having a little unmixed pumice at both ends. Barium carbonate was selected to multiply surface, as being a rather heavy powder that would not shrink nor fuse, nor be likely to decompose.

About 450 cc. of sixty per cent. acid = 270 grams of absolute acid were passed, in vapor, in three and five-tenths hours, into this mixture, heated as before. The distillate in the first, hot flask was eighty-one cc. of acid water of only one and six-tenths per cent. = one and three-tenths grams absolute acid. In the second ice-bath flask was 227 cc. sp. gr. about 0.955, containing one and two-tenths per cent. acid = two and seven-tenths grams absolute acid. Of the 270 grams passed in, four grams only distilled over unchanged, while 266 grams were decomposed. The 227 cc. of distillate in the second flask contained about 23.3 per cent. of acetone. This proportion gives about twenty per cent. of acetone from the 266 grams of absolute acid used. The stream of inflammable gases was very much greater than in the other experiments, burning with an almost continuous large flame.

The desired splitting of acetic acid to yield acetone requires two molecules of the acid to yield one molecule of acetone, the residuary products being one molecule each of carbon dioxide and water. That is, 120 grams of absolute acetic acid should give

58	grams of acetone,
44	" " carbon dioxide,
18	" " water, or

by percentage the acid should give

48.33	per cent.	acetone,
36.67	"	carbon dioxide,
15.00	"	water.

When marsh-gas or methane ( $\text{CH}_4$ ) and carbon monoxide ( $\text{CO}$ ) are formed it is probably largely, if not entirely, through a secondary decomposition of the acetone by a higher heat than that which gives the primary decomposition into acetone, carbon dioxide, and water, and when acetone and methane are produced together, it is rational to suppose that inequalities of heating are the cause. That is, if acetone be produced it indicates that the exact conditions required are present at that time and place. Then it follows that if these exact conditions be extended throughout the whole time and place of reaction the acetone splitting of the acid only can occur, and no methane or other products of other reactions can be produced. The conditions for producing these different reactions are doubtless different degrees of heating, and uniformity of reaction can be expected only from uniformity of heating. And the differences in the degrees of heat required to produce the different reactions here, do not seem to be great.

The physical and mechanical conditions of heating a stationary tube can not possibly yield an equal degree of heating to the contents of such a tube, especially where only a part of such contents is in motion. Even if the whole outside of the tube could be equally heated—as it could not be practically—the contents would be cooler from circumference to center. But in this case, where a current of vapor at about  $100^\circ \text{C.}$  is passed continually, into a tube the outside of which is kept unequally heated to  $500^\circ$  or  $600^\circ \text{C.}$ , and where this current has to find its way at varying speed through varying friction and expansion, only a varying decomposition can be possible, and the conclusion must be that if uniform decomposition is to be reached it must be through uniform conditions.

Equable heating in a stationary tube, under the conditions of this process, being impracticable, it became necessary to devise some better form of still; and a careful consideration of the principles involved, and the especial mechanical difficulties of this

decomposition, led the writer to a form of rotary still, which, after some alterations and modifications, has proved successful.

A wrought-iron tube about thirty-six cm. (fourteen inches) long by 12.7 cm. (five inches) in diameter, contracted at the ends to central hollow journals of about two cm. (three-fourths inch) external diameter and one and two-tenths cm. (five-tenths inch) bore, free to revolve, was supported in the center of the eighteen cm. (seven inches) drain-pipe furnace and connected at one end with the vapor supply and the other with the condensers by air-tight glands or "stuffing-boxes." The ends were provided with charging and discharging openings which could be closed air-tight, and the still was revolved slowly by means of a pulley on one end of the hollow shaft. A small stationary tube passed into the still through the revolving shaft to convey the acid vapor to the entrance of the still at one end, and a similar tube gave exit to the products of the decomposition at the other, condenser end. It was necessary to protect this tube from obstruction by dust carried by the current of vapors, and this was done by a cartridge of rolled up, wire cloth, filled with glass wool. This rotary still was driven at the rate of three to six revolutions per minute by a small water-motor, and was found to heat with great equability as it revolved over the burners. Inside of the still, at equal distances apart on the periphery, five L-shaped, longitudinal strips of sheet iron were riveted. These were necessary to prevent the charge from sliding round as the iron became smooth, and they were found to carry the charge round, turn it over, and mix it most effectively at each revolution. Thus, while by the revolutions over the source of heating the shell was heated very uniformly, this continuous moving and turning over of the contents must bring all parts of the charge, solids and vapors alike, in successive contact with the hot surfaces and the cooler atmosphere of the still, and thus secure a fair degree of equable heating. The still being about one-third filled with the solid charge and slowly rotated, the charge occupies principally,—not the bottom of the still directly over the fire, but the ascending third which has just been over the fire. Then, as the charge is carried up, the superficial cooler portion, too deep to be held by the longitudinal shelves, slides back upon the hot surface below,

while the portion carried on by the shelves falls back, shelf by shelf, from contact with the hot shell through the atmosphere of vapor, upon the cooler portions below to be mixed and carried up again in a similar order. At the same time the whole atmosphere of the still is filled with dust which becomes very fine, and very largely multiplies the surfaces of contact with the vapor, for decomposition, whilst the vapors pass slowly and uniformly and with a minimum of friction to the exit at the condenser end. If the motion and heating of a charge in this still be compared with those in a stationary still with a horizontal stirrer driven by a vertical shaft, the advantages of the former will be easily understood. The latter moves the charge round over the fire, but has a comparatively slight effect in bringing new portions of the charge successively in contact with the heating surfaces, and it does not tend to prevent horizontal stratification of the charge with consequent irregular heating; and it does not tend to the fullest contact of the vapors with the surfaces of the charge, where the decomposition probably takes place. After the inevitable number of trials and adjustments and breakings down, the following successful experiments are selected from a large number.

(4) As a parallel experiment to (1) with the stationary still, the rotary still was used empty.

About 200 cc. of thirty-six per cent. acid = seventy-two grams of absolute acid was slowly passed into the heated, rotating, empty still.

The first hot flask of distillate contained thirty-three cc. of acid of 14.6 per cent. = 4.82 grams absolute acid.

The second ice-bath flask contained 142 cc. of acid acetone 12.6 per cent. = 17.89 grams absolute acid. Then  $4.82 + 17.89 = 22.71$  grams absolute acid distilled over unchanged. Then seventy-two grams —  $22.71 = 49.29$  grams of acid decomposed. The second distillate gave an estimate of 12.1 grams acetone. Then as 49.29 acid : 12.1 acetone :: 100 : 24.5 per cent. acetone from the acid. The current of inflammable gas was considerable, but less than in (1).

(5) The rotary still was charged with about a liter of the same granulated pumice used in (2), and when heated about 295 cc

of sixty per cent. acid = 177 grams of absolute acid was passed in, in vapor during three and five-tenths hours.

The first distillate, hot flask, had 108 cc. of acid water of four and four-tenths per cent. = 4.75 grams acid.

The second distillate, ice-bath flask, had 116 cc. acid acetone two and four-tenths per cent. acid = 2.78 grams acid.

Then  $4.75 + 2.78 = 7.53$  grams acid came over unchanged, out of 177 grams passed in; or,  $177 - 7.53 = 169.47$  grams decomposed.

The acetone estimated by iodoform was 24.3 per cent. of the acid decomposed.

(6) About 500 grams of precipitated barium carbonate was put into the rotary still on top of the charge of pumice, and when the whole was heated, 380 cc. sixty per cent. acid = 288 grams of absolute acid was passed in, in vapor during three and five-tenths hours.

The first distillate was 108 cc. of acid water containing three and nine-tenths grams acid.

The second distillate was 135 cc. of acid acetone containing two and seven-tenths grams acid.

228 grams acid — six and six-tenths grams over unchanged = 221.4 grams decomposed.

The estimated acetone was sixteen per cent. of the acid decomposed.

Much inflammable gas throughout the process.

(7) About 456 grams of precipitated barium carbonate put into the cleaned-out rotary still, and when heated 510 cc. of thirty-six per cent. acid = 183.6 grams absolute acid was passed in, in four and five-tenths hours. About 24.5 grams of acid came over unchanged, leaving 159.1 grams, decomposed.

The acetone was estimated at 53.7 grams, or about thirty-four per cent. of the decomposed acid.

(8) Charged the rotary still with 1000 grams of dry barium acetate and distilled this acetate as long as it would yield a distillate, and until it was reduced to 770 grams of barium carbonate quite free from acetate. This yielded acetone estimated by iodoform at about sixty per cent of the theoretical quantity.

When the distillation from the acetate had ceased the receivers were changed and 490 cc. of sixty per cent. acid = 294 grams

of absolute acid were passed into this charge of carbonate in about four and five-tenths hours.

The distillate was received in five fractions.

1st.	37 cc. of acid water containing	15.6 per cent. acid or	5.77 grams.
2nd.	256 " " dilute acetone "	4.4 " " " "	11.26 "
3rd.	230 " " " " "	9.6 " " " "	22.08 "
4th.	46 " " " " "	11.0 " " " "	5.06 "
5th.	26 " " " " "	17.6 " " " "	4.58 "

595 cc.

Distilled over undecomposed, 48.75 grams.

294 grams—forty-nine grams = 245 grams decomposed.

In each of the second and third flasks was about forty cc. of water at the start. Then eighty from 595 gave 515 cc. of total distillate from the 490 cc. fed in.

Acetate required from 245 grams acid 118 grams. Estimated yield seventy-one gram or sixty per cent. of the required yield.

On the following day, without having opened the still, it was reheated and 530 cc. of sixty per cent. acid = 318 grams of absolute acid was passed in, in vapor. From low street pressure in the gas-mains the heat on this day was deficient.

1st distillate	50 cc. acid water containing	19.6 per cent. acid or	9.8 grams.
2d	" 255 " dilute acetone "	10.0 " " " "	25.5 "
3d	" 138 " " " "	6.0 " " " "	8.3 "

443 cc.

43.6 grams.

318 grams—forty-four grams = 274 grams acid decomposed.

Acetone required from 274 grams acid 132 grams. Estimated yield ninety-five grams or seventy-two per cent. of the required yield.

On the day following, again without opening the still, in about four hours, passed in 535 cc. of sixty per cent. acid = 321 grams of absolute acid.

1st dis., hot flask,	22 cc. acid water containing	7.6 per cent. acid or	1.67 gms.
2d	" ice-bath, 258 " dilute acetone "	4.8 " " " "	12.38 "
3d	" " 131. " " " "	7.6 " " " "	9.96 "

411 cc.

24.01 gms.

321 grams—twenty-four grams = 297 grams acid decomposed.

Acetone required by theory from 296 grams acid 143 grams. Obtained by estimate about 113 grams or nearly eighty per cent. of the required yield.

Now, upon cooling and opening the still, samples taken from various parts of the contents were all found to be barium carbonate and free from acetic acid.

During the progress of these distillations from punice stone, from carbonates, and from the empty stills alike, whenever the supply of acid vapor was cut off the distillation almost instantly ceased, showing that there was then nothing in the still to decompose.

This, then, is the improved, continuous process for the production of acetone directly from acetic acid, which avoids and saves the intermediate steps of forming and decomposing acetates.

The formation of acetates in the still was repeatedly tried with both barium and calcium carbonates, but always failed until the temperature was reduced to about the boiling-point of water, or the condensing-point of watery vapor, and then the acetates formed, cohered and adhered to the ribs and shell of the still, and no longer moved until again decomposed by a higher heat.

Corresponding trials were made with calcium carbonate and with calcium acetate decomposed to carbonate, with results very similar to those above given, but the barium carbonate seemed to answer best, possibly because it yields a heavier powder that occupies less space and moves better.

When commercial calcium acetate was used, tarry matters obstructed the exit tubes and contaminated the distillates. The portion of these tarry matters that was reduced to charcoal in the still, and there mixed with the carbonate, seemed to be rather beneficial than obstructive. But on the whole the process appeared to do better with carbonates reduced from acetates that were made for the purpose from good materials. As the process seems to be rather a mechanical or physical one of surface contact, it would be reasonable to expect better results from reduced carbonates than from precipitated carbonates. And it is still an open question whether, on the large manufacturing

scale, with better control of the essentials, heat and motion, pumice or bone black, or some other such substance, will not be better than the carbonates. Of one thing the writer is quite convinced, and that is that the close regulation of the heating within narrow limits of variation, is far the most important element in the process. Within very narrow limits, too little heat gives undecomposed acid, while too much gives inflammable gases in place of acetone. But on the large scale this element will be under much better control, whilst a proportionately longer still will give the acid vapor farther to go and a prolonged exposure to the limited heating and contact.

There are no patents sought for on this process or apparatus.

The dilute acetone from this process is fairly good and clean, and is colorless except for the action of the free acid contained on the iron tubing. With the free acid the specific gravity by hydrometer varies between 0.93 and 0.97. No part of the distillate has more than a thin film of oil on the surface too small to be measured, and this oily surface is only in the first flask with the acid water. On further dilution of the ice-bath distillate it is rendered opalescent for a minute or two and then becomes again transparent.

This distillate (undiluted) is a good solvent for many substances, and is probably pure enough for the manufacture of chloroform.

When allowed to stand some days upon caustic lime and then poured off and rectified, it is much improved in character and strength, and is then adapted to a still larger number of uses, and is perhaps better adapted to the manufacture of chloroform.

The product of this first rectification was then digested with about ten per cent. of dry calcium chloride. This abstracted most of the water and settled in dense solution at the bottom of the bright yellowish acetone. This latter was separated and distilled, and again digested for several days with ten per cent. of fresh calcium chloride, being frequently well shaken. Again twice separated and distilled from fresh portions of calcium chloride, in a capacious flask with a good Hempel tube filled with small glass marbles, and the whole apparatus filled with well-dried air, and distilled directly into specific gravity bottles, such as are described in the *Ephemeris*, 4, 1448—it gave six



fractions, four of which had the specific gravities at  $1\frac{1}{2}^{\circ}\text{C.}$ , as follows: First, 0.79662; second, 0.79704; third, 0.79712; sixth, 0.79793. The irregularities of these differences are doubtless due to differences in rate of boiling, yet they demonstrate conclusively that the first fraction can not be anhydrous.

Authorities differ much as to the specific gravity of acetone. The lowest noticed is, given by W. H. Perkin, Ph.D., F. R. S., in the *J. Chem. Soc.*, 1884, 45, 478. He gives the specific gravity at  $1\frac{1}{2}^{\circ}$  as 0.79652, and at  $2\frac{1}{2}^{\circ}$  as 0.78669—and says this is lower than that usually observed, but agrees pretty closely with that of Linnemann, who obtained  $1\frac{1}{2}^{\circ}=0.7975$ . Thorpe's number, calculated for this temperature, gave  $1\frac{1}{2}^{\circ}=0.80244$ . Judging from the circumstance that the writer's fractions did not agree, and that therefore there was no constant boiling-point to his distillate, and hence no part anhydrous—his and Perkin's results are both too high.

Notwithstanding this, the writer accepts, for the present at least, his own result as a basis for the following specific gravities of dilutions. His best results as obtained by the use of his above-mentioned specific gravity bottles, and a sensitive thermometer in tenths of a degree, recently compared with a standard, are as follows:

At  $\frac{1}{2}^{\circ}\text{C.}$  0.808157. At  $1\frac{1}{2}^{\circ}\text{C.}$  0.796620. At  $2\frac{1}{2}^{\circ}\text{C.}$  0.786988.

It was first desirable to know whether dilutions of acetone with water were mere mixtures, or whether as in the case of alcohol there was molecular combination with contraction and elevation of temperature. It was found that when forty cc. of acetone of about ninety per cent. was mixed with forty cc. of water there was a contraction of three and two-tenths cc., and an increase of temperature of  $5.6^{\circ}\text{C.}$ , with an effervescence of gas as in alcohol.

The proportion of ten grams of recently boiled distilled water added to ninety grams of this distillate, mixed by connecting two flasks with the weighed quantities, and passing the liquids back and forth without exposure to external air or loss of vapor, gave the following specific gravities:

Acetone at  $\frac{1}{2}^{\circ}\text{C.}$  0.8371.  $1\frac{1}{2}^{\circ}\text{C.}$  0.8260.  $2\frac{1}{2}^{\circ}\text{C.}$  0.8168 for ten per cent. of water, or ninety per cent. acetone.

This method of dilution by weighing the acetone and water separately in flasks and then connecting the flasks for mixing without loss of vapor or outer air contact was adopted for the basis of the following Acetone Table. The lines of the table that are given in heavy-faced type are given from actual observation, and the remainder by interpolation.

Acetone =  $C_2H_4O$ , or dimethyl ketone =  $CH_3COCH_3$ , is a transparent, colorless, mobile, light, inflammable liquid of an agreeable spirituous or ethereal odor, with a suggestion of mint, and a sharp, biting taste. The suggestion of mint in the odor varies in strength in different samples, and probably does not belong to acetone, but comes from a minute trace of impurity. It boils at  $56.3^\circ C.$  (Regnault). The specific gravity when very nearly anhydrous is at  $\frac{4}{4}^\circ C.$  0.808157, at  $\frac{15}{15}^\circ C.$  0.796620, at  $\frac{25}{25}^\circ C.$  0.786988. It mixes in all proportions with alcohol and water, and is a very general solvent, dissolving many substances that are insoluble in alcohol.

## ACETONE TABLE.

The lines of figures in broad-faced type are given from actual observation. The remainder of the table is interpolated.

The Acetone assumed for the basis of the table was not absolutely anhydrous, though probably very nearly so.

In the percentages no account is taken of the weight of the gases liberated on mixing acetone with water.

SPECIFIC GRAVITY AT			Percent- age by weight.	SPECIFIC GRAVITY AT			Percent- age by weight.
$\frac{4}{4}^\circ C.$	$\frac{15}{15}^\circ C.$	$\frac{25}{25}^\circ C.$		$\frac{4}{4}^\circ C.$	$\frac{15}{15}^\circ C.$	$\frac{25}{25}^\circ C.$	
0.8082	0.7966	0.7870	100	0.8524	0.8425	0.8338	84
0.8111	0.7995	0.7900	99	0.8549	0.8453	0.8366	83
0.8139	0.8025	0.7930	98	0.8575	0.8481	0.8394	82
0.8168	0.8054	0.7959	97	0.8600	0.8508	0.8422	81
0.8197	0.8084	0.7989	96	0.8626	0.8536	0.8450	80
0.8226	0.8113	0.8019	95	0.8651	0.8561	0.8476	79
0.8255	0.8142	0.8049	94	0.8676	0.8587	0.8502	78
0.8284	0.8172	0.8079	93	0.8701	0.8612	0.8528	77
0.8313	0.8201	0.8109	92	0.8726	0.8637	0.8554	76
0.8342	0.8231	0.8138	91	0.8752	0.8663	0.8580	75
0.8371	0.8260	0.8168	90	0.8777	0.8688	0.8605	74
0.8397	0.8288	0.8196	89	0.8802	0.8714	0.8631	73
0.8422	0.8315	0.8225	88	0.8827	0.8739	0.8657	72
0.8448	0.8343	0.8253	87	0.8852	0.8764	0.8683	71
0.8473	0.8370	0.8281	86	0.8877	0.8790	0.8709	70
0.8498	0.8398	0.8309	85	0.8900	0.8813	0.8732	69

SPECIFIC GRAVITY AT				SPECIFIC GRAVITY AT			
$\frac{4^\circ}{4^\circ}$ C.	$\frac{15^\circ}{15^\circ}$ C.	$\frac{25^\circ}{25^\circ}$ C.	Percent- age by weight.	$\frac{4^\circ}{4^\circ}$ C.	$\frac{15^\circ}{15^\circ}$ C.	$\frac{25^\circ}{25^\circ}$ C.	Percent- age by weight.
0.8923	0.8836	0.8756	68	0.9469	0.9392	0.9332	43
0.8946	0.8858	0.8779	67	0.9489	0.9412	0.9353	42
0.8969	0.8881	0.8803	66	0.9508	0.9433	0.9375	41
0.8992	0.8904	0.8826	65	0.9527	0.9454	0.9397	40
0.9014	0.8927	0.8850	64	0.9541	0.9469	0.9413	39
0.9037	0.8950	0.8874	63	0.9554	0.9484	0.9430	38
0.9060	0.8973	0.8897	62	0.9567	0.9499	0.9446	37
0.9083	0.8996	0.8921	61	0.9580	0.9514	0.9462	36
0.9106	0.9019	0.8944	60	0.9594	0.9529	0.9479	35
0.9129	0.9041	0.8968	59	0.9607	0.9544	0.9495	34
0.9151	0.9064	0.8991	58	0.9620	0.9559	0.9512	33
0.9174	0.9087	0.9015	57	0.9634	0.9574	0.9528	32
0.9197	0.9110	0.9038	56	0.9647	0.9589	0.9545	31
0.9220	0.9133	0.9062	55	0.9660	0.9604	0.9561	30
0.9243	0.9156	0.9086	54	0.9674	0.9619	0.9578	29
0.9266	0.9179	0.9109	53	0.9687	0.9635	0.9594	28
0.9289	0.9202	0.9133	52	0.9700	0.9650	0.9611	27
0.9311	0.9224	0.9156	51	0.9714	0.9665	0.9627	26
0.9334	0.9247	0.9180	50	0.9727	0.9680	0.9644	25
0.9354	0.9268	0.9202	49	0.9740	0.9795	0.9660	24
0.9373	0.9289	0.9223	48	0.9754	0.9710	0.9677	23
0.9392	0.9309	0.9245	47	0.9767	0.9725	0.9693	22
0.9411	0.9330	0.9267	46	0.9780	0.9740	0.9709	21
0.9431	0.9351	0.9288	45	0.9794	0.9755	0.9726	20
0.9450	0.9371	0.9310	44				

## REPORT OF COMMITTEE ON ATOMIC WEIGHTS, PUBLISHED DURING 1894.<sup>1</sup>

By F. W. CLARKE.

Received January 8, 1895.

*To the Members of the American Chemical Society:*

YOUR committee upon atomic weights respectfully submits the following report, which summarizes the work done in this department of chemistry during 1894. Although the volume of completed determinations is not large, it is known that several important investigations are in progress, from which valuable results may be expected in the near future. It is in this country that the greatest activity exists, and that the greatest progress is being made at present; and the preparation of these reports is therefore a peculiarly appropriate function of the Society. The data for 1894 are as follows:

*The H:O ratio.*—An interesting attempt at the indirect measurement of this ratio, which is the base line upon which our sys-

<sup>1</sup> Read at the Boston Meeting, December 28, 1894.

tem of atomic weights depends, has been made by Julius Thomsen.<sup>1</sup> His determinations are really determinations of the ratio  $\text{NH}_3 : \text{HCl}$ , and were conducted thus: First, pure, dry, gaseous hydrochloric acid was passed into a weighed absorption apparatus containing pure distilled water. After noting the increase in weight, gaseous ammonia was passed through to slight excess, and the apparatus was weighed again. The excess of ammonia was then measured by titration with standard hydrochloric acid. In weighing, the apparatus was tared by another as nearly like it as possible, containing the same amount of water. Three sets of weighings were made, with apparatus of different size, and these Thomsen considers separately, giving the greatest weight to the experiments involving the largest masses of material. The data are as follows, with the ratio  $\frac{\text{HCl}}{\text{NH}_3}$  in the third column:

## FIRST SERIES.

Wt. HCl.	Wt. $\text{NH}_3$ .	Ratio
5.1624	2.4120	2.1403
3.9425	1.8409	2.1416
4.6544	2.1739	2.1411
3.9840	1.8609	2.1409
5.3295	2.4898	2.1406
4.2517	1.9863	2.1405
4.8287	2.2550	2.1414
6.4377	3.0068	2.1411
4.1804	1.9528	2.1407
5.0363	2.3523	2.1410
4.6408	2.1685	2.1411

## SECOND SERIES.

Wt. HCl.	Wt. $\text{NH}_3$ .	Ratio.
11.8418	5.5302	2.14130
14.3018	6.6808	2.14073
12.1502	5.6759	2.14067
11.5443	5.3927	2.14073
12.3617	5.7733	2.14118

## THIRD SERIES.

Wt. HCl.	Wt. $\text{NH}_3$ .	Ratio.
19.3455	9.0360	2.14094
19.4578	9.0890	2.14081

<sup>1</sup>*Ztschr. phys. Chem.*, 13, 398.

From the sums of the weights Thomsen finds the ratio to be 2.14087, or 2.13934 in vacuo. From this, using Ostwald's reduction of Stas' data for the atomic weights of nitrogen and chlorine, he gets the ratio  $O : H :: 16 : 0.99946$ , or almost exactly  $16 : 1$ . In a later paper<sup>1</sup> Thomsen himself recalculates Stas' data, with  $O = 16$  as the basis of computation, and derives from them the subjoined values for the elements which Stas studied:

Ag.....	107.9299
Cl .....	35.4494
Br .....	79.9510
I .....	126.8556
S .....	32.0606
Pb.....	206.9042
K .....	39.1507
Na.....	23.0543
Li .....	7.0307
N .....	14.0396

Combining these values for chlorine and nitrogen with his ratio  $HCl : NH_3$ , he gets  $O : H :: 16 : 0.9992$ . This, however, is only an apparent support of Prout's hypothesis, for it depends upon the anti-Proutian determinations of Stas. If we calculate from Thomsen's new ratio with  $N = 14$  and  $Cl = 35.5$ , it gives  $H = 1.0242$ ; which is most unsatisfactory. In short, the method followed by Thomsen is too indirect and subject to too many possibilities of error to entitle it to much weight in fixing so important a constant as the atomic weight of oxygen. The direct processes, followed by several recent investigators, and giving  $O = 15.87$  to  $15.89$  are much more trustworthy. Meyer and Seubert<sup>2</sup>, in their criticism of Thomsen's work, have pointed out some of its uncertainties.

In this connection it may be noted that Scott's research upon the composition of water by volume, cited by abstract in the report of last year, has been published in full in the *Philosophical Transactions*.<sup>3</sup>

**Strontium.**—The atomic weight of strontium has been re-determined by Richards<sup>4</sup> from analyses of the bromide. The first ratio measured, after a careful preliminary study of materials

<sup>1</sup> *Ztschr. phys. Chem.*, 13, 726.

<sup>2</sup> *Ber d. chem. Ges.*, 27, 2770. See also abstract by Ostwald in *Ztschr. phys. Chem.*, 15, 705.

<sup>3</sup> 1894, 543, 1893.

<sup>4</sup> *Proc. Amer. Acad.* 1894, 369.

and methods, was that between silver and strontium bromide. Of this ratio, three sets of determinations were made, all volumetric, but with differences of detail in the process. The weights are as follows, with the ratio  $\text{Ag}_2:\text{SrBr}_2::100:x$  in the third column:

FIRST SERIES.		
Wt. Ag.	Wt. SrBr <sub>2</sub> .	Ratio.
1.30755	1.49962	114.689
2.10351	2.41225	114.677
2.23357	2.56153	114.683
5.36840	6.15663	114.683
<hr/>		
Sum, 11.01303	12.63003	114.683

SECOND SERIES.		
Wt. Ag.	Wt. SrBr <sub>2</sub> .	Ratio.
1.30762	1.49962	114.683
2.10322	2.41225	114.693
4.57502	5.24727	114.694
5.36800	6.15663	114.691
<hr/>		
Sum, 13.35386	15.31577	114.692

THIRD SERIES.		
Wt. Ag.	Wt. SrBr <sub>2</sub> .	Ratio.
2.5434	2.9172	114.697
3.3957	3.8946	114.692
3.9607	4.5426	114.692
4.5750	5.2473	114.695
<hr/>		
Sum, 14.4748	16.6017	114.694

From these data we have, if  $\text{Ag} = 107.93$ , and  $\text{Br} = 79.955$ , ( $\text{O} = 16$ ), the following results:

From first series.....	$\text{Sr} = 87.644$
" second series.....	87.663
" third series.....	87.668

In two additional series, partly identical with the foregoing, the silver bromide thrown down was collected and weighed. I subjoin the weighings with the ratio  $2\text{AgBr}:\text{SrBr}_2$  in the last column.

FIRST SERIES.		
2AgBr.	SrBr <sub>2</sub> .	Ratio.
2.4415	1.6086	65.886
2.8561	1.8817	65.884
6.9337	4.5681	65.883
<hr/>	<hr/>	<hr/>
Sum, 12.2313	8.0584	65.8834

## SECOND SERIES.

2AgBr.	SrBr <sub>2</sub> .	Ratio.
2.27625	1.49962	65.881
3.66140	2.41225	65.883
3.88776	2.56153	65.887
9.34497	6.15663	65.882
Sum, 19.17038	12.63003	65.883

From the first series..... Sr = 87.660

" " second series..... 87.659

The average of all five series is Sr = 87.659.

*Barium*.—Richards has corroborated his earlier determinations of the atomic weight of barium, which were made with the bromide, by means of additional series of experiments upon the chloride.<sup>1</sup> The work was carried out in the most elaborate and thorough manner, and for details the original paper must be consulted. First, barium chloride was titrated with standard solutions of silver, and the several series represent different methods of ascertaining accurately the end point. The data are as follows, with the ratio Ag, : BaCl<sub>2</sub> :: 100 : x in the third column.

## FIRST SERIES.

Wt. Ag.	Wt. BaCl <sub>2</sub> .	Ratio.
6.1872	5.9717	96.517
5.6580	5.4597	96.495
3.5988	3.4728	96.499
9.4010	9.0726	96.507
0.7199	0.6950	96.541

Mean, 96.512

## SECOND SERIES.

Wt. Ag.	Wt. BaCl <sub>2</sub> .	Ratio.
6.59993	6.36974	96.512
5.55229	5.36010	96.539
4.06380	3.92244	96.522

Mean, 96.524

## THIRD SERIES.

Wt. Ag.	Wt. BaCl <sub>2</sub> .	Ratio.
4.4355	4.2815	96.528
2.7440	2.6488	96.531
6.1865	5.9712	96.520
3.4023	3.2841	96.526

Mean, 96.526

<sup>1</sup> *Proc. Amer. Acad.*, 29, 55.

## FOURTH SERIES.

Wt. Ag.	Wt. BaCl <sub>2</sub> .	Ratio.
6.7342	6.50022	96.525
10.6023	10.23365	96.523

Mean, 96.524

All the weights represent vacuum standards. From the four series the atomic weight of barium is deduced as follows; when  $O = 16$ .

First series .....	Ba = 137.419
Second " .....	137.445
Third " .....	137.449
Fourth " .....	137.445

In three more series of experiments Richards determined the ratio between  $2AgCl$  and  $BaCl_2$ . The data are subjoined, with the ratio  $2AgCl : BaCl_2 :: 100 : x$  appended.

## FIRST SERIES.

Wt. AgCl.	Wt. BaCl <sub>2</sub> .	Ratio.
8.7673	6.3697	72.653
5.1979	3.7765	72.654
4.9342	3.5846	72.648
2.0765	1.5085	72.646
4.4271	3.2163	72.650

Mean, 72.649

## SECOND SERIES.

Wt. AgCl.	Wt. BaCl <sub>2</sub> .	Ratio.
2.09750	1.52384	72.650
7.37610	5.36010	72.669
5.39906	3.92244	72.650

Mean, 72.6563

## THIRD SERIES.

Wt. AgCl.	Wt. BaCl <sub>2</sub> .	Ratio.
8.2189	5.97123	72.6524
4.5199	3.28410	72.6587

Mean, 72.6555

Hence we have for Ba,

First series.....	Ba = 137.428
Second " .....	" = 137.446
Third " .....	" = 137.444

The mean of all is 137.440, as against 137.434 found in the work on the bromide. By combining the two chloride ratios,



Ag, BaCl, and 2AgCl : BaCl<sub>2</sub>, the ratio Ag : Cl can be computed. This gives Ag = 107.930, a value identical with that of Stas.

*Cobalt and Nickel.*—The atomic weights of these two metals have been redetermined by Winkler,<sup>1</sup> who adopts a radically new method, using the pure electrolytic elements as a starting-point. In each case, the weighed metal, deposited upon platinum, is treated with a weighed excess of iodine dissolved in potassium iodide. The metals are thus converted into iodides, and the excess of iodine is then measured by titration with thio-sulphate solution. Thus the direct ratios, Co : I, Ni : I, are determined. Two series of estimations are given for each metal, with results as follows. The atomic weights used in calculation are H = 1, I = 126.53.

## FIRST SERIES—COBALT.

Wt. Co.	Wt. I.	At. Wt. Co.
0.4999	2.128837	59.4242
0.5084	2.166750	59.3772
0.5290	2.254335	59.3828
0.6822	2.908399	59.3582
0.6715	2.861617	59.3824

Mean, 59.3849

## SECOND SERIES—COBALT.

0.5185	2.209694	59.3798
0.5267	2.246037	59.3430
0.5319	2.268736	59.3294

Mean, 59.3507

Mean of all, Co = 59.3678.

## FIRST SERIES—NICKEL.

Wt. Ni.	Wt. I.	At. Wt. Ni.
0.5144	2.217494	58.6702
0.4983	2.148502	58.6918
0.5265	2.268742	58.7268
0.6889	2.970709	58.6828
0.6876	2.965918	58.6678

Mean, 58.6878

## SECOND SERIES—NICKEL.

0.5120	2.205627	58.7436
0.5200	2.204107	58.7432
0.5246	2.259925	58.7432

Mean, 58.7433

<sup>1</sup> *Ztschr. anorg. Chem.*, 8, 1.

Mean of all, Ni = 58.7155.

For O = 16, these become

Co = 59.517

Ni = 58.863.

*Palladium*.—In 1889 Keiser published his determinations of the atomic weight of palladium, for which, since then, other investigators have found somewhat different values. He has now, jointly with Mary B. Breed, given a new set of determinations, which confirm his former series.<sup>1</sup> As before, palladium-ammonium chloride was reduced in hydrogen, the salt being prepared by two methods and carefully examined as to purity. Two series of experiments are given, with the following weights of material :

#### FIRST SERIES.

Pd(NH <sub>4</sub> Cl) <sub>2</sub> .	Pd.	At. Wt. Pd.
1.60842	0.80997	106.271
2.08295	1.04920	106.325
2.02440	1.01975	106.334
2.54810	1.28360	106.342
1.75505	0.88410	106.341

From sum of weights, 106.325

Reduced to vacuum, 106.246

#### SECOND SERIES.

Pd(NH <sub>4</sub> Cl) <sub>2</sub> .	Pd.	At. Wt. Pd.
1.50275	0.75685	106.297
1.23672	0.62286	106.296
1.34470	0.67739	106.343
1.49059	0.75095	106.353

From sum of weights, 106.322

Reduced to vacuum, 106.245

The atomic weight was computed with H = 1, N = 14.01, and Cl = 35.37. If O = 16 this becomes Pd = 106.51. This is only 0.02 less than the value obtained in the earlier investigation.

*Tungsten*.—A new determination of the atomic weight of tungsten, by Pennington and Smith,<sup>2</sup> leads to a much higher value than that commonly accepted. The older work seems very probably to have been done upon material contaminated

<sup>1</sup> *Am. Chem. J.*, 16, 20.

<sup>2</sup> Read before the Amer. Philos. Soc., Nov. 2, 1894.

with molybdenum, an impurity which was eliminated in this investigation by Debray's method,—that is, by volatilization by means of gaseous hydrochloric acid. The metal, carefully purified, was oxidized in porcelain crucibles, with all necessary precautions, and the following data are given:

Wt. W.	Wt. O <sub>2</sub> .	At. Wt. W.
0.862871	0.223952	184.942
0.650700	0.168900	184.923
0.597654	0.155143	184.909
0.666820	0.173103	184.902
0.428228	0.111168	184.900
0.671920	0.174406	184.925
0.590220	0.153193	184.933
0.568654	0.147588	184.943
1.080973	0.280600	184.913

Mean, 184.921

All weights are reduced to a vacuum, and O = 16 is taken as the standard of reference.

Another paper, by Smith and Desi, was read at the same meeting with that just cited. In this research, the tungstic oxide was purified in the same way, and reduced by heating in a stream of pure hydrogen. The water formed was weighed, and all weights reduced to a vacuum. Computed with O = 16 and H = 1.008, the results are as follows:

Wt. WO <sub>3</sub> .	Wt. H <sub>2</sub> O.	At. Wt. W.
0.983024	0.22834	184.683
0.998424	0.23189	184.709
1.008074	0.23409	184.749
0.911974	0.21184	184.678
0.997974	0.23179	184.704
1.007024	0.23389	184.706

Mean, 184.704

Why this result should be lower than that previously found by Pennington and Smith remains to be explained.

**Thallium.**—Two determinations of atomic weight were made by Wells and Penfield to ascertain the constancy of the element 'such.' The nitrate was fractionally crystallized until about the twentieth remained in the mother-liquor, while another

twentieth had been subjected to repeated recrystallization. Both fractions were converted into thallium chloride, which was dried at  $100^{\circ}$ , and in both the chlorine was estimated by weighing as silver chloride on a Gooch filter. The results were as follows:

	TlCl.	AgCl.	At. Wt. Tl.
Crystals.....	3.9146	2.3393	204.47
Mother-liquor.....	3.3415	1.9968	204.47

Calculated with  $\text{Ag} = 107.92$  and  $\text{Cl} = 35.45$ .

In the report for 1893 Lepierre's work on thallium was given, and the last value cited was  $\text{Tl} = 203.00$ , varying widely from the rest of the series, and affecting the mean. The mean stated by Lepierre was 203.62, and as found by me was 203.57. Lepierre<sup>1</sup> now calls attention to the fact that his value 203.00 was a misprint for 203.60, and that his mean was therefore correctly given. He also gives additional details relative to his work.

*Bismuth.*—The long-standing controversy between Schneider and Classen over the atomic weight of bismuth, has led to a new set of determinations on the part of Schneider.<sup>2</sup> The old method was still used; namely, of converting the metal into the trioxide by means of nitric acid and subsequent ignition of the nitrate; but the metal itself was carefully purified. Results as follows:

Wt. Bi.	Wt. $\text{Bi}_2\text{O}_3$ .	Per cent. Bi in $\text{Bi}_2\text{O}_3$ .
5.0092	5.5868	89.661
3.6770	4.1016	89.648
7.2493	8.0854	89.659
9.2479	10.3142	89.662
6.0945	6.7979	89.653
12.1588	13.5610	89.660

Mean, 89.657

If  $\text{O} = 16$ , Bi ranges from 207.94 to 208.15, or in mean 208.05, confirming the earlier determinations.

*Tin.*—Incidentally to his paper on the white tin sulphide Schmidt gives one determination of the atomic weight of the metal.<sup>3</sup>

0.5243 gram Sn gave 0.6659  $\text{SnO}_2$ . Hence  $\text{Sn} = 118.48$ .

<sup>1</sup> *Bull. Soc. Chim.*, [3], 11, 423.

<sup>2</sup> *J. prakt. Chem.*, [2], 50, 461.

<sup>3</sup> *Ber d. chem. Ges.*, 27, 2713.

*Anomalous Nitrogen.*—An important discovery has been made by Lord Rayleigh, who finds that nitrogen obtained by purely chemical methods is perceptibly lighter than that from atmospheric air.<sup>1</sup> Equal volumes of the gas, variously prepared, weighed as follows:

By passing NO over hot iron.....	2.30008
“ “ N <sub>2</sub> O “ “ “ .....	2.29904
“ “ AmNO <sub>2</sub> “ “ “ .....	2.29869

For nitrogen from air he found:

From air passed over hot iron.....	2.31003
“ “ “ through moist FeO, H <sub>2</sub> .....	2.31020
“ “ “ over hot copper .....	2.31026

Investigating the cause of this anomaly, with the co-operation of Ramsay, Rayleigh came to the astonishing results communicated a few months later to the British Association. It was found, in short, that atmospheric air contains a gas heavier than nitrogen, and hitherto unknown. Its density, in a sample as pure as could be obtained, was 19.09, and it was characterized by extraordinary inertness. Whether it is a new element, or allotropic nitrogen, N<sub>2</sub>, remains to be determined. The work is cited here because it shows that the density of nitrogen as hitherto determined, can give no trustworthy value for the atomic weight of the element.

*Miscellaneous Notes.*—Some data bearing upon the atomic weight of tellurium are given by Gooch and Howland.<sup>2</sup> As the homogeneity of tellurium is still uncertain, I omit their details.

Wanklyn's attempt to show that the atomic weight of carbon is not 12, but 6, was noted last year. He has since published more on the subject in a paper on Russian Kerosene,<sup>3</sup> and the matter was also discussed at the Oxford meeting of the British Association.<sup>4</sup>

In a communication upon the Stasian determinations,<sup>5</sup> Hinrichs discusses the availability of silver as a secondary standard in the scale of atomic weights. He makes silver, chlorine, bromine, iodine, and sulphur all Proutian in value. Hinrichs also

<sup>1</sup> *Chem. News*, 69, 231, May 18, 1894.

<sup>2</sup> *Am. J. Sci.*, [3], 48, 375.

<sup>3</sup> *Phil. Mag.*, [5], 37, 495.

<sup>4</sup> *Chem. News*, 70, 87, Aug. 24, 1894.

<sup>5</sup> *Compt. rend.*, 118, 528.

has published his views upon atomic weights *in extenso* in book form.<sup>1</sup>

In conclusion I submit a table of atomic weights revised to January 1, 1894. O = 16 is still retained as the base of the system; but I hope that in another year it will be practicable to return to H = 1.

Name.	Atomic Weight.	Name.	Atomic Weight.
Aluminum.....	27.	Neodymium.....	140.5
Antimony .....	120.	Nickel .....	58.7
Arsenic .....	75.	Nitrogen.....	14.03
Barium.....	137.43	Osmium.....	190.8
Bismuth .....	208.	Oxygen .....	16.
Boron .....	11.	Palladium .....	106.5
Bromine .....	79.95	Phosphorus .....	31.
Cadmium.....	112.	Platinum.....	195.
Caesium .....	132.9	Potassium.....	39.11
Calcium .....	40.	Praseodymium .....	143.5
Carbon .....	12.	Rhodium .....	103.
Cerium .....	140.2	Rubidium .....	85.5
Chlorine.....	35.45	Ruthenium.....	101.6
Chromium.....	52.1	Samarium .....	150.
Cobalt .....	59.5	Scandium .....	44.
Columbium .....	94.	Selenium.....	79.
Copper .....	63.6	Silicon .....	28.4
Erbium.....	166.3	Silver .....	107.92
Fluorine.....	19.	Sodium .....	23.05
Gadolinium .....	156.1	Strontium.....	87.66
Gallium .....	69.	Sulphur .....	32.06
Germanium .....	72.3	Tantalum .....	182.6
Glucinum .....	9.	Tellurium .....	125.
Gold .....	197.3	Terbium .....	160.
Hydrogen .....	1.008	Thallium.....	204.18
Indium.....	113.7	Thorium .....	232.6
Iodine .....	126.85	Thulium .....	170.7
Iridium.....	193.1	Tin.....	119.
Iron .....	56.	Titanium .....	48.
Lanthanum.....	138.2	Tungsten.....	184.9
Lead.....	206.95	Uranium .....	239.6
Lithium .....	7.02	Vanadium .....	51.4
Magnesium .....	24.3	Ytterbium.....	173.
Manganese .....	55.	Yttrium .....	89.1
Mercury .....	200.	Zinc.....	65.3
Molybdenum .....	96.	Zirconium.....	90.6

<sup>1</sup> The True Atomic Weight of the Chemical Elements, and the Unity of Matter. By Gustavus Detlef Hiurichs, St. Louis, 1894.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY, U. S. DEPARTMENT  
OF AGRICULTURE, SENT BY H. W. WILEY, No. 13.]

## COLORING MATTER IN THE CALIFORNIA RED WINES.<sup>1</sup>

BY W. D. BIGELOW.

Received January 8, 1895.

**D**URING the last three quarters of a century the coloring matter of red wines has been carefully investigated. Those undertaking the work have endeavored to find some reaction or series of reactions, by which the natural coloring matter of the grape could be distinguished from that of other fruit and vegetables with which wines are so frequently adulterated. The introduction of the aniline colors into this industry attracted for a time a portion of the attention which had previously been given entirely to the vegetable colors, and methods have been brought forward by which the former can be recognized. On account of the comparative ease and certainty with which the aniline colors can be detected, wine makers still give their preference to the vegetable pigments, and a method for their detection is still regarded as desirable. A large number of methods have been suggested for this purpose, but most of them have proved worthless, and none of them at all satisfactory.

Among the difficulties which have been encountered by workers in this field, and which have not yet been overcome, are the following:

1. Many of the substances employed for coloring wines are so nearly identical with the natural coloring matter of the grape that it would not be an easy matter to distinguish between them even in freshly prepared solutions.

2. The coloring matter of wine changes materially with age, and different reactions are given by samples of the same variety and from the same locality, but of different vintages.

3. Different reactions are commonly obtained with wines of the same age, but of different varieties or from different parts of the country.

<sup>1</sup> Read before the Washington Section in abstract, November 8, 1894, and before the American Chemical Society, December 27, 1894.

As an example of the difficulties which are met with in making use of any of the methods that have been brought forward, let us notice the action of lead subacetate. According to Vögel this reagent gives a grayish green precipitate with pure wines, while with wines colored with elderberries, the juice of beets, &c., a precipitate colored indigo-blue, red, or some equally characteristic color is obtained. A more careful examination of the method revealed the fact that a number of fortified wines known to be free from foreign coloring matter gave distinct red and violet precipitates, while elderberries and mallow added to some of the lighter wines could not be detected. The same difficulties are experienced to a greater or less extent in all methods which have been suggested, and it is now customary in examining a wine for foreign vegetable coloring matter, to compare it with a wine of known purity, of the same variety, the same vintage, and from the same locality, as the sample under examination.

This work with California wines was done under the direction of Dr. H. W. Wiley, and was in connection with the examination made during the past year of the samples furnished by the California Viticultural Association. In all, ninety-four samples of California red wines were examined. Their age varied from one to seven years.

No wines were available which were known to be colored with vegetable pigments, and the facilities for coloring them were lacking, since wines colored after fermentation are quite different from those fermented after the addition of colored vegetable material to the must. This work was not undertaken, therefore, with the hope of developing a method for the detection of foreign coloring matter in wine, but merely for the purpose of studying the coloring matter of California wines, and of recording the reactions given by some of the reagents, whose reactions with the European wines have been the subject of so much careful study. The number of reagents employed was limited by the size of the samples.

For convenience the methods which were employed are divided into three classes. The methods given in the first class give a red, blue, or violet color with wines containing foreign



coloring matter, and usually a green or grayish green tint when the wines are pure.

The second class of reagents includes certain metallic oxides, such as manganese dioxide and lead dioxide. These have been used in different proportions, sometimes to distinguish between natural wines and those colored with foreign vegetable colors, sometimes between the vegetable colors and coal-tar colors in wine. They have not been found entirely satisfactory, since the amount necessary to decolorize some pure wines is sufficient to destroy even the aniline colors in some that had been artificially colored. Yet they have been found of great assistance in the examination of such wines as claret and burgundy. These reagents were found to destroy almost all the color in California wines when used in the proportions recommended for French claret and similar wines.

The third class includes methods which use chalk treated with albumen and charged with various reagents.

#### CLASS I.

*Lead Acetate—Neutral and Basic.*—The reactions obtained with neutral and basic lead acetate were almost identical. The precipitates were yellowish green, grayish green, gray or brown. No blue, red, or violet colors were obtained.

*Sodium Carbonate.*—In the use of this reagent the solution recommended by Gautier (*Sophistication et analyse des vins*, 4me. edition, page 211) was employed. One cc. of wine was mixed with five cc. of a five-tenths per cent. solution of sodium carbonate. The colors obtained were brown, yellowish brown, and yellowish to grayish green.

*Sodium Bicarbonate.*—Gautier's solution was also employed with this reagent. Eight grams of sodium bicarbonate were dissolved in 100 cc. of water and the solution saturated with carbon dioxide. Equal volumes of this solution and the wine under examination were mixed and the color noted. The reactions obtained were gray or grayish green, with sometimes a tinge of brown.

*Ammonia.*—The action of dilute ammonia on red wine was first pointed out by Chevallier in 1827, and since then it has been commonly used in their examination. The solution used in this

work contained one part of strong ammonia to nine parts of water. This was then added to wine in equal volumes, and the resulting mixture was filtered when turbid. The filtrates were colored various shades of brown and green with an occasional orange-red.

*Ammonium Hydroxide and Ammonium Sulphhydroxide.*—A mixture of twenty cc. of ammonium hydroxide and eight cc. of ammonium sulphhydroxide were diluted with water to one liter, and a portion of five cc. treated with an equal volume of wine. The resulting solutions were brown to yellowish brown.

*Alum and Potassium Carbonate.*—Five cc. of a saturated solution of ammonia alum were mixed with ten cc. of wine, five cc. of a one-tenth solution of potassium carbonate added, and the whole stirred and filtered. The precipitates were gray or yellowish brown with sometimes a tinge of green. The filtrates were sometimes of a light wine color, but were not lilac or wine-colored in any case.

*Alum and Lead Acetate.*—This method is the same as the preceding except that a one-tenth solution of lead acetate is used instead of potassium carbonate. The precipitates were colored yellowish gray to brown except in three cases, when they were of a light wine color.

*Borax.*—Two volumes of a saturated solution of borax were mixed with one of wine. A brown to yellowish brown color was obtained with all wines except one sample of Gutedel, which gave an orange-red color.

*Copper Sulphate.*—Ten cc. of wine were diluted with water to 100 cc. and thirty cc. of a saturated solution of copper sulphate added. The color of the solution was changed in every case to a light olive-green.

*Tartar Emetic.*—Two to three volumes of wine were mixed with one volume of a saturated solution of tartar emetic. The color was changed in every case to a bright cherry-red.

#### CLASS 2.

*Manganese Dioxide.*—100 cc. of wine were shaken for fifteen minutes with fifteen grams of manganese dioxide, and the mixture filtered. The filtrates were light colored, but were not entirely decolorized in any case. Shaking the filtrates with

another portion of fifteen grams of maganese dioxide rendered them almost colorless.

*Lead Peroxide.*—Five grams of lead peroxide were added to twenty cc. of wine, and the mixture well shaken and filtered. Some of the filtrates were entirely decolorized, though in many of them a very light wine color remained.

*Mercuric Oxide.*—Ten cc. of wine were shaken for one minute with three-tenths to four-tenths gram precipitated mercuric oxide (Cazeneuve uses one to one and one-half grams) and filtered. The filtrates were all colorless or light yellow.

#### CLASS 3.

*Sodium Peroxide.*—M. Ruisand uses sodium peroxide to detect aniline coloring matters in wine. He adds ten to fifteen cc. of sodium peroxide to five cc. of wine, allows it to stand twenty minutes, and renders slightly acid with acetic acid. According to Ruisand, both vegetable colors and aniline derivatives are decolorized by the peroxide, while the coal-tar colors are restored by acetic acid.

With the California wines the color is not entirely destroyed, even with twice the quantity of peroxide recommended by Ruisand, and in many cases a marked wine color remained both before and after acidification.

A lump of chalk was cut into pieces about fifteen mm. square and half as thick, and one side of each piece was carefully smoothed with a knife. These pieces of chalk were then immersed for two hours in a ten per cent. solution of egg albumen and dried at 45°. They were then divided into five portions, one of which was reserved for testing the wine without further treatment, and each of the other four immersed for forty minutes in a one per cent. solution of one of the following reagents: Tartar emetic, lead acetate, copper acetate, and zinc acetate. After being dried at 50°, they are ready for use. Three drops of each wine examined were placed on the smooth surface of one block from each of the five divisions given above, the blocks dried at 100° for one hour, and the color noted. Another block from each division was treated with the same amount of wine, dried for twenty-four hours at the temperature of the laboratory, and the color compared with that of the blocks dried at 100°. The colors

obtained were brown, grayish brown, and slate colored. No tinge of violet, blue, or green, was obtained in any case. In every case the color of the block dried at  $100^{\circ}$  was almost, if not exactly, identical with that of the block treated with the same wine and dried at the temperature of the laboratory.

According to the reactions obtained with these reagents, the coloring matter of California wines appears to be much more uniform than that of European wines. The reactions are not always the same as those obtained with the more ordinary European wines; for instance, a gray, or yellowish, or orange-gray precipitate or solution is sometimes obtained with reagents which are said to give green or grayish green with French wines. On the other hand no reactions were obtained which are said to be characteristic of wines colored with vegetable pigments.

### THE PENETRATION MACHINE—AN EXPLANATION.

BY H. C. BOWEN.

Received January 24, 1895.

ON page 59, January number, 1895, of this JOURNAL, a somewhat vague reference is made to a testing instrument. The identity of the instrument referred to is made manifest to me by the context. The instrument is known by those who have to do with it as the Penetration Machine; first described in print by myself in the School of Mines Quarterly, 10, 297, under the title "An Apparatus for Determining the Relative Degree of Cohesion of a Semi-Liquid Body." The reference above noted, by some mischance, does the instrument and its work injustice. The origin of the instrument was due to pressing needs in the technology of asphalt cements used for paving purposes. These cements, made by different parties using different tempering agents, were very varied, and at the time of the origin of this instrument there was no way other than chewing the cement for foremen to test whether the cement was of required consistency or not. Since that time (1889) thousands of tons of cement have been manufactured, and the whole of this cement has been strictly tested by this machine with nicety and satisfaction. These cements are made in all parts of the country, to a certain penetration number, previously determined as necessary according to the different uses of the cement.

Without this control cements would be used that were not suited for the purpose designed, and much damage would be occasioned in different cities, which damage would much cripple the asphalt paving industry. Cargoes of cement are shipped, one requirement of the cement being that it shall have a certain penetration number previously determined by the contracting parties. Since the introduction of this testing apparatus many qualities of cement have been studied and others discovered. By it we have learned the influence of mild or sudden and marked changes of temperatures, and the consequence of severe cold. It enables us to learn the influence of hardening and softening agents, a matter of great importance in the practical uses of asphalt cement. Thus it is manifest that this instrument has an important and serious part to perform in a great industry, and that its use is far from being an idle pastime.

SCHOOL OF MINES, COLUMBIA COLLEGE,  
N. Y. CITY, JANUARY 23, 1895.

---

### NOTES.

*Argon: A New Constituent of the Atmosphere.*—At the meeting of the Royal Society, held on January 31, the long-expected paper by Lord Rayleigh and Professor Ramsay was read, and a full report has just been received by way of *The Chemical News*, of February 1, from which the following condensed summary is taken: A careful comparison of the nitrogen from urea, ammonium nitrite, and from nitrous and nitric oxid—"chemical nitrogen" with atmospheric nitrogen was made, and gave a weight per liter for

Chemical nitrogen of.....	1.2505 grams
Atmospheric " .....	1.2572 "

Nitrogen which had been extracted from the air by means of magnesium was separated also and gave a figure differing inappreciably from that recorded above for "chemical nitrogen." The nitrogen contained in magnesium nitride was also converted into ammonium chloride and this was found to contain exactly the proportion of chlorine contained in ordinary ammonium chloride. From this it was concluded that red-hot magnesium withdraws from "atmospheric nitrogen" no substance other than nitrogen capable of forming a basic compound with hydrogen. After having endeavored in every way possible to detect in "atmospheric nitrogen" known gases to account for the difference in specific gravity the authors finally repeated Cavendish's experiment. It will be remembered that Cavendish found that when air to which oxygen was added, the electric spark passed for several days and the nitrous and nitric acids

<sup>1</sup> See also page 211 of this issue.

removed by soap-lees and finally the oxygen removed by liver of sulphur that "only a small bubble of air remained unabsorbed which certainly was not more than the  $\frac{1}{175}$  of the bulk of the phlogisticated air let up into the tube; so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest, and can not be reduced to nitrous acid, we may safely conclude that it is not more than  $\frac{1}{175}$  part of the whole." Improving the apparatus of Cavendish so as to shorten the duration of the experiment Rayleigh and Ramsay found that fifty cc. of air left 0.32 cc. of gas. On adding this residue to a fresh fifty cc. of air and repeating the operation the residue now amounted to 0.76 cc.

By passing nitrogen over magnesium turnings contained in a heated tube, 1,500 cc. unabsorbed gas was obtained and after passing this for several days over soda-lime, phosphoric anhydride, magnesium at a red heat, and copper oxide, the gas was reduced to 200 cc. and its density found to be 16.1. After further absorption the density was increased to 19.09. On passing sparks for several hours through a mixture of a small quantity of this gas with oxygen, its volume was still further reduced. Assuming that this reduction was due to the further elimination of nitrogen the density of the remaining gas was calculated to be 20.0.

By means of atmolysis using long clay pipe-stems the amount of argon was increased in the air, which finally passed from the pipes so that the nitrogen in it weighed in a total weight of approximately two and three-tenths grams a mean of 0.00187 gram over that of the same volume of "atmospheric nitrogen." By increasing the efficiency of the apparatus the excess was in mean 0.0035 gram.

Experiments then made to prove the absence or presence of argon in chemical nitrogen showed that three liters of chemical nitrogen from ammonium nitrite left three and three-tenths cc. of argon, a part of which is accounted for by an accident. In a second experiment 5,660 cc. of the same nitrogen left three and five-tenths cc. argon. The source of this was found in the water used for confining the gases which absorbs argon from the air in considerable amount, and again gives it up to the confined gases. The amount of argon obtained from the chemical nitrogen was less than  $\frac{1}{40}$  of the normal amount from atmospheric nitrogen. The following quotations from the paper of Rayleigh and Ramsay and from those of Crookes and Olszewski, which followed it, are scarcely susceptible of condensation:

#### *Separation of Argon on a Large Scale.*

To prepare argon on a large scale, air is freed from oxygen by means of red-hot copper. The residue is then passed from a gas-holder through a combustion tube, heated in a furnace, and containing copper, in order to remove all traces of oxygen; the issuing gas is then dried by passage over soda-lime and phosphorus pentoxide, after passage through a small U tube containing sulphuric acid, to indicate the rate of flow. It then enters a combustion tube packed tightly with magnesium turnings, and heated

to redness in a second furnace. From this tube it passes through a second index-tube, and enters a small gas-holder capable of containing three or four liters. A single tube of magnesium will absorb from seven to eight liters of nitrogen. The temperature must be nearly that of the fusion of the glass, and the current of gas must be carefully regulated, else the heat developed by the union of the magnesium with nitrogen will fuse the tube.

Having collected the residue from 100 to 150 liters of atmospheric nitrogen, which may amount to four or five liters, it is transferred to a small gas-holder connected with an apparatus, whereby, by means of a species of a self-acting Sprengel's pump, the gas is caused to circulate through a tube half filled with copper and half with copper oxide; it then traverses a tube half filled with soda-lime and half with phosphorus pentoxide; it then passes a reservoir of about 300 cc. capacity, from which, by raising a mercury reservoir, it can be expelled into a small gas-holder. Next it passes through a tube containing magnesium turnings heated to bright redness. The gas is thus freed from any possible contamination with oxygen, hydrogen, or hydrocarbons, and nitrogen is gradually absorbed. As the amount of gas in the tubes and reservoir diminishes in volume it draws supplies from the gas-holder, and, finally, the circulating system is full of argon in a pure state. The circulating system of tubes is connected with a mercury pump, so that, in changing the magnesium tube, no gas may be lost. Before ceasing to heat the magnesium tube the system is pumped empty, and the collected gas is restored to the gas-holder; finally, all the argon is transferred from the mercury reservoir to the second small gas-holder, which should preferably be filled with water saturated with argon, so as to prevent contamination from oxygen or nitrogen; or, if preferred, a mercury gas-holder may be employed. The complete removal of nitrogen from argon is very slow towards the end, but circulation for a couple of days usually effects it.

The principal objection to the oxygen method of isolating argon, as hitherto described, is the extreme slowness of the operation. In extending the scale we had the great advantage of the advice of Mr. Crookes, who not long since called attention to the flame rising from platinum terminals, which convey a high tension alternating electric discharge, and pointed out its dependence upon combustion of the nitrogen and oxygen of the air.<sup>1</sup> The plant consists of a De Meritens alternator, actuated by a gas engine, and the currents are transformed to a high potential by means of a Ruhmkorff or other suitable induction coil. The highest rate of absorption of the mixed gases yet attained is three liters per hour, about 3,000 times that of Cavendish. It is necessary to keep the apparatus cool, and from this and other causes a good many difficulties have been encountered.

In one experiment of this kind, the total air led in after seven days' working, amounted to 7,925 cc., and of oxygen (prepared from potassium

<sup>1</sup> *Chemical News*, 65, 301, 1892.

chlorate), 9137 cc. On the eighth and ninth days oxygen alone was added, of which about 500 cc. was consumed, while there remained about 700 cc. in the flask. Hence the proportion in which the air and oxygen combined was as 79:96. The progress of the removal of the nitrogen was examined from time to time with the spectroscope, and became ultimately very slow. At last the yellow line disappeared, the contraction having apparently stopped for two hours. It is worthy of notice that with the removal of the nitrogen, the arc discharge changes greatly in appearance, becoming narrower and blue rather than greenish in color.

The final treatment of the residual 700 cc. of gas was on the model of the small scale operations, already described. Oxygen or hydrogen could be supplied, at pleasure, from an electrolytic apparatus, but in no way could the volume be reduced below sixty-five cc. This residue refused oxidation and showed no trace of the yellow line of nitrogen, even under favorable conditions.

When the gas stood for some days over water, the nitrogen line reasserted itself in the spectrum, and many hour's sparking with a little oxygen was required again to get rid of it. Intentional additions of air to gas free from nitrogen showed that about one and one-half per cent. was clearly, and about three per cent. was conspicuously, visible. About the same numbers apply to the visibility of nitrogen in oxygen when sparked under these conditions, that is, at atmospheric pressure, and with a jar connected to the secondary terminals.

*Density of Argon prepared by means of Oxygen.*

A first estimate of the density of argon prepared by the oxygen method was founded upon the data already recorded respecting the volume present in air, on the assumption that the accurately known densities of atmospheric and of chemical nitrogen differ on account of the presence of argon in the former, and that during the treatment with oxygen nothing is oxidized except nitrogen. Thus, if

$D$  = density of chemical nitrogen,

$D'$  = " " atmospheric nitrogen,

$d$  = " " argon,

$a$  = proportional volume of argon in atmospheric nitrogen,

the law of mixtures give—

$$ad + (1-a)D = D',$$

or—

$$d = D + (D' - D)/a.$$

In this formula  $D' - D$  and  $a$  are both small, but they are known with fair accuracy. From the data already given—

$$a = \frac{65}{0.79 \times 7925}$$

whence if (on an arbitrary scale of reckoning)  $D = 2.2990$ ,  $D' = 2.3102$ , we find  $d = 3.378$ . Thus if  $N_2$  be 14, or  $O_2$  be 16, the density of argon is 20.6.

A direct determination by weighing is desirable, but hitherto it has not



been feasible to collect by this means sufficient to fill the large globe employed for other gases. A *mixture* of about 400 cc. of argon with pure oxygen, however, gave the weight 2.7315, 0.1045 in excess of the weight of oxygen, *viz.*, 2.6270. Thus, if  $a$  be the ratio of the volume of argon to the whole volume, the number for argon will be—

$$2.6270 + 0.1045/a.$$

The value of  $a$ , being involved only in the excess of weight above that of oxygen, does not require to be known very accurately. Sufficiently concordant analyses by two methods gave  $a = 0.1845$ ; whence for the weight of the gas we get 3.193, so that, if  $O_2 = 16$ , the density of the gas would be 19.45. An allowance for residual nitrogen, still visible in the gas before admixture of oxygen, raises this number to 19.7, which may be taken as the density of pure argon resulting from this determination.

#### *Density of Argon prepared by means of Magnesium.*

The density of the original sample of argon prepared has already been mentioned. It was 19.09; and, after sparking with oxygen, it was calculated to be 20.0. The most reliable results of a number of determinations give it as 19.90. The difficulty in accurately determining the density is to make sure that all nitrogen has been removed. The sample of density 19.90 showed no spectrum of nitrogen when examined in a vacuum tube. It is right, however, to remark that the highest density registered was 20.38. But there is some reason here to distrust the weighing of the vacuum globe.

#### *Spectrum of Argon.*

The spectrum of argon, seen in a vacuum tube of about three mm. pressure consists of a great number of lines, distributed over almost the whole visible field. Two lines are specially characteristic; they are less refrangible than the red lines of hydrogen or lithium, and serve well to identify the gas, when examined in this way. Mr. Crookes, who will give a full account of the spectrum in a separate communication, has kindly furnished us with the accurate wave-lengths of these lines, as well as of some others next to be described; they are respectively 696.56 and 705.64,  $10^{-6}$  mm.

Besides these red lines, a bright yellow line, more refrangible than the sodium line, occurs at 603.84. A group of five bright green lines occurs next, besides a number of less intensity. Of the group of five, the second, which is perhaps the most brilliant, has the wave-length 561.00. There is next a blue or blue violet line of wave-length 470.2; and last, in the less easily visible part of the spectrum, there are five strong violet lines, of which the fourth, which is the most brilliant, has the wave-length 420.0.

Unfortunately, the red lines, which are not to be mistaken for those of any other substance, are not easily seen when a jar discharge is passed through argon at atmospheric pressure. The spectrum seen under these conditions has been examined by Professor Schuster. The most charac-

teristic lines are perhaps those in the neighborhood of F, and are very easily seen if there be not too much nitrogen, in spite of the presence of some oxygen and water vapor. The approximate wave-lengths are—

487.91.....	Strong.
[486.07] .....	F.
484.71.....	Not quite so strong.
480.52.....	Strong.
476.50.....	} Fairly strong characteristic triplet.
473.53.....	
472.56.....	

It is necessary to anticipate Mr. Crookes' communication, and to state that when the current is passed from the induction coil in one direction, that end of the capillary tube next the positive pole appears of a redder, and that next the negative pole of a bluer hue. There are, in effect, two spectra, which Mr. Crookes has succeeded in separating to a considerable extent. Mr. E. C. Baly,<sup>1</sup> who has noticed a similar phenomenon, attributes it to the presence of two gases. He says: "When an electric current is passed through a mixture of two gases, one is separated from the other and appears in the negative glow." The conclusion would follow that what we have termed "argon" is in reality a mixture of two gases which have as yet not been separated. This conclusion, if true, is of great importance, and experiments are now in progress to test it by the use of other physical methods. The full bearing of this possibility will appear later.

The presence of a small quantity of nitrogen interferes greatly with the argon spectrum. But we have found that in a tube with platinum electrodes, after the discharge has been passed for four hours, the spectrum of nitrogen disappears, and the argon spectrum manifests itself in full purity. A specially constructed tube with magnesium electrodes, which we hoped would yield good results, removed all traces of nitrogen, it is true; but hydrogen was evolved from the magnesium, and showed its characteristic lines very strongly. However, these are easily identified. The gas evolved on heating magnesium *in vacuo*, as proved by a separate experiment, consists entirely of hydrogen.

Mr. Crookes has proved the identity of the chief lines of the spectrum of gas separated from air-nitrogen by aid of magnesium with that remaining after sparking the air-nitrogen with oxygen in presence of caustic soda solution.

Prof. Schuster has also found the principal lines identical in the spectra of the two gases, as observed by the jar discharge at atmospheric pressure.

#### *Solubility of Argon in Water.*

Determinations of the solubility in water of argon prepared by sparking, gave 3.94 volumes per 100 of water at 12°. The solubility of gas pre-

<sup>1</sup> *Proc. Phys. Soc.*, 1893, p. 147.

pared by means of magnesium was found to be 4.05 volumes per 100 at 13.9°. The gas is therefore about two and one-half times as soluble as nitrogen, and possesses approximately the same solubility as oxygen.

The fact that argon is more soluble than nitrogen would lead us to expect it in increased proportion in the dissolved gases of rain-water. Experiment has confirmed this anticipation. "Nitrogen" prepared from the dissolved gases of water supplied from a rain-water cistern was weighed upon two occasions. The weights, corresponding to those recorded \* \* were 2.3221 and 2.3227, showing an excess of twenty-four mgms. above the weight of true nitrogen. Since the corresponding excess for "atmospheric nitrogen" is eleven mgms. we conclude that the water "nitrogen" is relatively more than twice as rich in argon.

On the other hand, gas evolved from the hot spring at Bath, and collected for us by Dr. A. Richardson, gave a residue after removal of oxygen and carbon dioxide, whose weight was only about midway between that of true and atmospheric nitrogen.

#### *Behavior at Low Temperatures.<sup>1</sup>*

Preliminary experiments, carried out to liquefy argon at a pressure of about 100 atmospheres, and at a temperature of -90°, failed. No appearance of liquefaction could be observed.

Professor Charles Olszewski, of Cracow, the well-known authority on the constants of liquefied gases at low temperatures, kindly offered to make experiments on the liquefaction of argon. His results are embodied in a separate communication, but it is allowable to state here that the gas has a lower critical-point and a lower boiling-point than oxygen, and that he has succeeded in solidifying argon to white crystals. The sample of gas he experimented with was exceptionally pure, and had been prepared by help of magnesium. It showed no trace of nitrogen when examined in a vacuum tube.

#### *Ratio of Specific Heats.*

In order to decide regarding the elementary or compound nature of argon, experiments were made on the velocity of sound in it. It will be remembered that, from the velocity of sound in a gas, the ratio of specific heat at constant pressure to that at constant volume can be deduced by means of the equation—

$$n\lambda = v = \sqrt{\left\{ \frac{e}{d} (1 + at) \frac{C_p}{C_v} \right\}},$$

when  $n$  is the frequency,  $\lambda$  the wave-length of sound,  $v$  its velocity,  $e$  the isothermal elasticity,  $d$  the density,  $(1 + at)$  the temperature correction,  $C_p$  the specific heat at constant pressure, and  $C_v$  that at constant volume. In comparing two gases at the same temperature, each of which obeys Boyle's law with sufficient approximation, and in using the same sound,

<sup>1</sup> The arrangements for the experiments upon this branch of the subject were left entirely in Professor Ramsay's hands.

many of these terms disappear, and the ratio of specific heats of one gas may be deduced from that of the other, if known, by means of the proportion—

$$\lambda^3 d : \lambda'^3 d' :: 1.41 : x,$$

where, for example,  $\lambda$  and  $d$  refer to air, of which the ratio is 1.41, according to observations by Röntgen, Wüllner, Kayser, and Jamin and Richard.

Two completely different series of observations, one in a tube of about two mm. diameter, and one in one of eight mm., made with entirely different samples of gas, gave, the first, 1.65 as the ratio, and, the second, 1.61.

Experiments made with the first tube, to test the accuracy of its working, gave for carbon dioxide the ratio 1.276, instead of 1.288, the mean of all previous determinations; and the half wave-length of sound in hydrogen was found to be 73.6, instead of 74.5, the mean of those previously found. The ratio of the specific heats of hydrogen found was 1.39, instead of 1.402.

There can be no doubt, therefore, that argon gives practically the ratio of specific heats, *viz.*, 1.66 proper to a gas in which all the energy is translational. The only other gas which has been found to behave similarly is mercury gas, at a high temperature.<sup>1</sup>

#### *Attempts to Induce Chemical Combination.*

Many attempts to induce argon to combine will be described in full in the complete paper. Suffice it to say here that all such attempts have as yet proved abortive. Argon does not combine with oxygen in presence of alkali under the influence of the electric discharge, nor with hydrogen in presence of acid or alkali also when sparked; nor with chlorine, dry or moist, when sparked; nor with phosphorus at a bright-red heat; nor with sulphur at bright redness. Tellurium may be distilled in a current of the gas; so may sodium and potassium, their metallic luster remaining unchanged. It is unabsorbed by passing it over fused red-hot caustic soda, or soda-lime heated to bright redness; it passes unaffected over fused and bright red-hot potassium nitrate; and red-hot sodium peroxide does not combine with it. Persulphides of sodium and calcium are also without action at a red heat. Platinum-black does not absorb it, nor does platinum sponge, and wet oxidizing and chlorinating agents, such as nitrohydrochloric acid, bromine water, bromine and alkali, and hydrochloric acid and potassium permanganate, are entirely without action. Experiments with fluorine are in contemplation, but the difficulty is great; and an attempt will be made to produce a carbon arc in the gas. Mixtures of sodium and silica and of sodium and boracic anhydride are also without action; hence it appears to resist attack by nascent silicon and by nascent boron.

#### *General Conclusions.*

It remains, finally, to discuss the probable nature of the gas, or mix-

<sup>1</sup> Kundt and Warburg, *Pogg. Ann.*, 135, 337 and 527.

ture of gases, which we have succeeded in separating from atmospheric air, and which we provisionally name *argon*.

The presence of argon in the atmosphere is proved by many lines of evidence. The high density of "atmospheric nitrogen," the lower density of nitrogen from chemical sources, and the uniformity in the density of samples of chemical nitrogen prepared from different compounds, lead to the conclusion that the cause of the anomaly is the presence of a heavy gas in air. If that gas possess the density twenty compared with hydrogen, "atmospheric" nitrogen should contain of it approximately one per cent. This is, in fact, found to be the case. Moreover, as nitrogen is removed from air by means of red-hot magnesium, the density of the remaining gas rises proportionately to the concentration of the heavier constituent.

*Second.*—This gas has been concentrated in the atmosphere by diffusion. It is true that it has not been freed from oxygen and nitrogen by diffusion, but the process of diffusion increases, relatively to nitrogen, the amount of argon in that portion which does not pass through the porous walls. This has been proved by its increase in density.

*Third.*—As the solubility of argon in water is relatively high, it is to be expected that the density of the mixture of argon and nitrogen, pumped out of water along with oxygen, should, after the removal of the oxygen, be higher than that of "atmospheric" nitrogen. Experiment has shown that the density is considerably increased.

*Fourth.*—It is in the highest degree improbable that two processes, so different from each other, should manufacture the same product. The explanation is simple if it be granted that these processes merely eliminate nitrogen from an "atmospheric" mixture. Moreover, as argon is an element, or a mixture of elements, its manufacture would mean its separation from one of the substances employed. The gas which can be removed from red-hot magnesium in a vacuum has been found to be wholly hydrogen. Nitrogen from chemical sources has been practically all absorbed by magnesium, and also when sparked in presence of oxygen; hence, argon can not have resulted from the decomposition of nitrogen. That it is not produced from oxygen is sufficiently borne out by its preparation by means of magnesium.

Other arguments could be adduced, but the above are sufficient to justify the conclusion that argon is present in the atmosphere.

The identity of the leading lines in the spectrum, the similar solubility and the similar density, appear to prove the identity of the argon prepared by both processes.

Argon is an element, or a mixture of elements, for Clausius has shown that if  $K$  be the energy of translatory motion of the molecules of a gas, and  $H$  their whole kinetic energy, then—

$$\frac{K}{H} = \frac{3(C_p - C_v)}{2C_v}$$

$C_p$  and  $C_v$  denoting as usual the specific heat at constant pressure and at

constant volume respectively. Hence if, as for mercury vapor and for argon, the ratio of specific heats  $C_p : C_v$  be  $1\frac{1}{2}$ , it follows that  $K=H$ , or that the whole kinetic energy of the gas is accounted for by the translatory motion of its molecules. In the case of mercury, the absence of interatomic energy is regarded as proof of the monatomic character of the vapor, and the conclusion holds equally good for argon.

The only alternative is to suppose that if argon molecules are di- or polyatomic, the atoms acquire no relative motion, even of rotation, a conclusion exceedingly improbable in itself, and one postulating the sphericity of such complex groups of atoms.

Now a monatomic gas can be only an element, or a mixture of elements; and hence, it follows that argon is not of a compound nature.

From Avogadro's law, the density of a gas is half its molecular weight; and as the density of argon is approximately twenty, hence, its molecular weight must be forty. But its molecule is identical with its atom; hence, its atomic weight, or, if it be a mixture, the mean of the atomic weights of that mixture, taken for the proportion in which they are present, must be forty.

There is evidence both for and against the hypothesis that argon is a mixture; for, owing to Mr Crooke's observations of the dual character of its spectrum; against, because of Professor Olszewski's statement that it has a definite melting-point, a definite boiling-point, and a definite critical temperature and pressure; and because, on compressing the gas in presence of its liquid, pressure remains sensibly constant until all gas has condensed to liquid. The latter experiments are the well-known criteria of a pure substance; the former is not known with certainty to be characteristic of a mixture. The conclusions which follow are, however, so startling that in our future experimental work we shall endeavor to decide the question by other means.

For the present, however, the balance of evidence seems to point to simplicity. We have, therefore, to discuss the relations to other elements of an element of atomic weight forty. We inclined for long to the view that argon was possibly one or more than one of the elements which might be expected to follow fluorine in the periodic classification of the elements—elements which should have an atomic weight between nineteen, that of fluorine, and twenty-three, that of sodium. But this view is completely put out of court by the discovery of the monatomic nature of its molecules.

The series of elements possessing atomic weights near forty are—

Chlorine .....	35.5
Potassium.....	39.1
Calcium.....	40.0
Scandium .....	44.0

There can be no doubt that potassium, calcium, and scandium follow legitimately their predecessors in the vertical columns, lithium, beryllium,

and boron, and that they are in almost certain relation with rubidium, strontium, and (but not so certainly) yttrium. If argon be a single element, then there is reason to doubt whether the periodic classification of the elements is complete; whether, in fact, elements may not exist which can not be fitted among those of which it is composed. On the other hand, if argon be a mixture of two elements, they might find place in the eighth group, one after chlorine and one after bromine. Assuming thirty-seven (the approximate mean between the atomic weights of chlorine and potassium) to be the atomic weight of the lighter element, and forty the mean atomic weight found, and supposing that the second element has an atomic weight between those of bromine, eighty, and rubidium, 85.5; *viz.*, eighty-two, the mixture should consist of 93.3 per cent. of the lighter, and six and seven-tenths per cent. of the heavier element. But it appears improbable that such a high percentage as six and seven-tenths of heavier element should have escaped detection during liquefaction.

If it be supposed that argon belongs to the eighth group, then its properties would fit fairly well with what might be anticipated. For the series, which contains—



might be expected to end with an element of monatomic molecules of no valency, *i. e.*, incapable of forming a compound, or if forming one, being an octad; and it would form a possible transition to potassium, with its monovalence, on the other hand. Such conceptions are, however, of a speculative nature; yet they may be, perhaps, excused, if they, in any way lead to experiments which tend to throw more light on the anomalies of this curious element.

In conclusion, it need excite no astonishment that argon is so indifferent to reagents. For mercury, although a monatomic element, forms compounds which are by no means stable at a high temperature in the gaseous state; and attempts to produce compounds of argon may be likened to attempts to cause combination between mercury gas at  $800^{\circ}$  and other elements. As for the physical condition of argon, that of a gas, we possess no knowledge why carbon, with its low atomic weight, should be a solid, while nitrogen is a gas, except in so far as we ascribe molecular complexity to the former and comparative molecular simplicity to the latter. Argon, with its comparatively low density and its molecular simplicity, might well be expected to rank among the gases. And its inertness, which has suggested its name, sufficiently explains why it has not previously been discovered as a constituent of compound bodies.

We would suggest for this element, assuming provisionally that it is not a mixture, the symbol A.

We have to record our thanks to Messrs. Gordon, Kallas, and Matthews, who have materially assisted us in the prosecution of this research.

Mr. Crookes (before reading his paper) said: Allow me, Mr. President, to take this opportunity of striking the key-note of the chorus of applause

and congratulations which will follow from all chemists present on this most valuable and important paper. The difficulties in a research of this kind are peculiar. Here we have a new chemical element, the principal properties of which seem to be the negation of all chemical properties. Chemists will understand how difficult it is to deal with anything which forms no compounds and unites with nothing. The discovery commenced by a prediction, followed after an interval by realization. Discoveries of this kind are more important and take a higher rank, than discoveries which, more or less, come in a haphazard sort of way. The prediction and discovery of argon are only equalled by the few discoveries of elements which have been made in chemistry by the careful study of the periodic law, and to surpass it we must go back to the predicted existence and subsequent discovery of an unknown planet by Adams and Leverrier.

*On the Spectra of Argon.* By William Crookes, F. R. S., etc. (Abstract.)

Through the kindness of Lord Rayleigh and Professor Ramsay I have been enabled to examine the spectrum of this gas in a very accurate spectroscope, and also to take photographs of its spectra in a spectrograph fitted with a complete quartz train.

Argon resembles nitrogen in that it gives two distinct spectra, according to the strength of the induction current employed. But while the two spectra of nitrogen are different in character, one showing fluted bands and the other sharp lines, the argon spectra both consist of sharp lines. It is, however, very difficult to get argon so free from nitrogen that it will not at first show the nitrogen flutings superposed on its own special system of lines. I have used argon prepared by Lord Rayleigh, Professor Ramsay, and myself, and however free it was supposed to be from nitrogen, I could always detect the nitrogen bands in its spectrum. These, however, soon disappear when the induction spark is passed through the tube for some time, varying from a few minutes to a few hours. The vacuum tubes best adapted for showing the spectra are of the ordinary Plücker form, having a capillary tube in the middle. For photographing the higher rays which are cut off by glass I have used a similar tube, "end on," having a quartz window at one end.

The pressure of argon giving the greatest luminosity and most brilliant spectrum is three mm. At this point the color of the discharge is an orange-red, and the spectrum is rich in red rays, two being especially prominent at wave-lengths 696.56 and 705.64. On passing the current the traces of nitrogen bands soon disappear, and the argon spectrum is seen in a state of purity. At this pressure the platinum from the poles spatters over the glass of the bulbs, owing to what I have called "electrical evaporation," and I think the residual nitrogen is absorbed by the finely-divided metal. Similar absorptions are frequently noticed by those who work much with vacuum tubes.

If the pressure is further reduced, and a Leyden jar intercalated in the

<sup>1</sup> *Roy. Soc. Proc.*, 1, 88, June, 1891.



circuit, the color of the luminous discharge changes from red to a rich steel blue, and the spectrum shows an almost entirely different set of lines. It is not easy to obtain the blue color and spectrum entirely free from the red. The red is easily got by using a large coil<sup>1</sup> actuated with a current of three amperes and six volts. There is then no tendency for it to burn blue.

The blue color may be obtained with the large coil by actuating it with a current of 3.84 amperes and eleven volts, intercalating a jar of fifty square inches surface. The make-and-break must be screwed up so as to vibrate as rapidly as possible. The red glow is produced by the positive spark, and the blue by the negative spark.

I have taken photographs of the two spectra of argon partly superposed. In this way their dissimilarity is readily seen.<sup>2</sup> In the spectrum of the blue glow I have counted 119 lines, and in that of the red glow eighty lines, making 199 lines in all; of these, twenty-six appear to be common to both spectra.

I have said that the residual nitrogen is removed by sparking the tube for some time when platinum terminals are sealed in. This is not the only way of purifying the argon. By the kindness of Professor Ramsay I was allowed to take some vacuum tubes to his laboratory and there exhaust and fill them with some of his purest argon. On this occasion I simultaneously filled, exhausted, and sealed off two Plücker tubes, one having platinum and the other aluminum terminals. On testing the gas immediately after they were sealed off, each tube showed the argon spectrum, contaminated by a trace of nitrogen bands. The next day the tube with platinum terminals was unchanged, but that having aluminum terminals showed the pure spectrum of argon, the faint nitrogen bands having entirely disappeared during the night. After an hour's sparking and a few days' rest the tube with platinum terminals likewise gave a pure argon spectrum. When a mixture of argon with a very little nitrogen is sparked in a tube made of pure fused quartz, without inside metallic terminals, the nitrogen bands do not disappear from the argon spectrum, but the spectra of argon and nitrogen continue to be seen simultaneously.

A vacuum tube was filled with pure argon and kept on the pump while observations were made on the spectrum of the gas as exhaustion proceeded. The large coil was used with a current of 8.84 amperes and eleven volts; no jar was interposed. At a pressure of three mm. the spectrum was that of the pure red glow. This persisted as the exhaustion rose, until at a pressure of about half a millimeter flashes of blue light made their appearance. At a quarter of a millimeter the color of the ignited gas was pure blue, and the spectrum showed no trace of the red glow.

<sup>1</sup> The coil used has about sixty miles of secondary wire, and when fully charged gives a torrent of sparks twenty-four inches long. The smaller coil gives six-inch sparks when worked with six half-pint Grove cells.

<sup>2</sup> Photographs of the different spectra of argon, and other gaseous spectra for comparison, were projected on the screen.

An experiment was now made to see if the small quantity of argon normally present in the atmosphere could be detected without previous concentration. Nitrogen was prepared from the atmosphere by burning phosphorus, and was purified in the usual manner. This gas, well dried over phosphoric anhydride, was passed into a vacuum tube, the air washed out by two fillings and exhaustions, and the tube was finally sealed off at a pressure of fifty-two mm. It was used for photographing the band spectrum of nitrogen on several occasions, and altogether it was exposed to the induction current from the large coil for eight hours before any change was noticed. The last time when photographing its spectrum difficulty was experienced in getting the spark to pass, so I increased the current and intercalated a small jar. The color immediately changed from the reddish yellow of nitrogen to the blue of argon, and on applying the spectroscope the lines of argon shone out with scarcely any admixture of nitrogen bands. With great difficulty and by employing a very small jar I was able to take one photograph of its spectrum and compare it with the spectrum of argon from Professor Ramsay, both being taken on the same plate, but the tube soon became non-conducting, and I could not then force a spark through, except by employing a dangerously large current. Whenever a flash passed it was of a deep blue color. Assuming that the atmosphere contains one per cent. of argon, the three mm. of nitrogen originally in the tube would contain 0.03 mm. of argon. After the nitrogen had been absorbed by the spattered platinum, this pressure of argon would be near the point of non-conduction.

In all cases when argon has been obtained in this manner the spectrum has been that of the blue-glowing gas. Very little of the red rays can be seen. The change from red to blue is chiefly dependent on the strength and heat of the spark: partly also on the degree of exhaustion. It is not improbable, and I understand that independent observations have already led the discoverers to the same conclusion—that the gas argon is not a simple body, but is a mixture of at least two elements, one of which glows red and the other blue, each having its distinctive spectrum. The theory that it is a simple body, has, however, support from the analogy of other gases. Thus, nitrogen has two distinct spectra, one or the other being produced by varying the pressure and intensity of the spark. I have made vacuum tubes containing rarefied nitrogen which show either the fluted band or the sharp line spectrum by simply turning the screw of the make-and-break, exactly as the two spectra of argon can be changed from one to the other.

I have prepared tubes containing other gases as well as nitrogen at different pressures, and have examined their spectra both by eye observation and by photography. The sharp line spectrum of nitrogen is not nearly so striking in brilliancy, number, or sharpness of lines as are those of argon, and careful scrutiny fails to show more than one or two apparent coincidences between lines in the two spectra. Between the spectra of argon and the band spectrum of nitrogen there are two or three close

approximations of lines, but a projection on the screen of a magnified image of the two spectra partly superposed will show that two at least of these are not real coincidences.

I have looked for indications of lines in the argon spectra corresponding to the corona line at wave-length 531.7, the aurora line at 557.1, and the helium line at 587.5, but have failed to detect any line of argon sufficiently near these positions to fall within the limits of experimental error.

I have found no other spectrum-giving gas or vapor yield spectra at all like those of argon, and the apparent coincidences in some of the lines which, on one or two occasions are noticed, have been very few, and would probably disappear on using a higher dispersion. As far, therefore, as spectrum work can decide, the verdict must be that Lord Rayleigh and Professor Ramsay have added one, if not two members to the family of elementary bodies.

*The Liquefaction and Solidification of Argon.* By Dr. K. Olszewski, Professor of Chemistry in the University of Cracow.

Having been furnished, by Professor Ramsay's kindness, with a sample of the new gas, argon, I have carried out experiments on its behavior at a low temperature and at high pressures, in order to contribute, at least in part, to the knowledge of the properties of this interesting body.

The argon sent by Professor Ramsay amounted to 300 cc. It was contained in a hermetically sealed glass bulb, so constructed that it could easily be transferred, with no appreciable loss, into the carefully dried and vacuum apparatus in which the proposed experiments were to be performed. The argon with which I was supplied, had, according to Professor Ramsay's statement, been dried with phosphoric anhydride; its density was 19.9 ( $H=1$ ); and he thought that at the outside it might contain one to two per cent. of nitrogen, although it showed no nitrogen spectrum when examined in a Plücker's tube.

Four series of experiments in all were carried out, two with the object of determining the critical temperature and pressure of argon, as well as measuring its vapor pressure at several other low temperatures, while two other series served to determine its boiling and freezing-points under atmospheric pressure, as well as its density at its boiling-point.

A detailed description of these experiments will be given in another place; I shall here give only a short description of the manner in which they were made.

For the first two experiments I made use of a Cailletet's apparatus. Its metallic manometer had been previously compared with the readings of a mercury manometer. As a cooling agent I used liquid ethylene, boiling under diminished pressure. The glass tube of Cailletet's apparatus was so arranged that the portion immersed in the liquid ethylene had comparatively thin walls (not exceeding one mm.), so as to equalize the external and internal temperature as quickly as possible.

In both the other experiments the argon was contained in a burette, closed at both ends with glass stop-cocks. By connecting the lower end

of the burette with a mercury reservoir, the argon was transferred into a narrow glass tube fused at its lower end to the upper end of the burette, and in which the argon was liquefied, and its volume in the liquid state measured. In these two series of experiments liquid oxygen, boiling under atmospheric or under diminished pressure, was employed as a cooling agent. I made use of a hydrogen thermometer in all these experiments to measure low temperatures.

*Determination of the Critical Constants of Argon.*

As soon as the temperature of liquid ethylene had been lowered to  $-128.6^{\circ}$ , the argon easily condensed to a colorless liquid under a pressure of thirty-eight atmospheres. On slowly raising the temperature of the ethylene, the meniscus of the liquid argon became less and less distinct, and finally vanished at the following temperatures and corresponding pressures :

Expt.	Temperature.	Pressure.
1.	$-121.2^{\circ}$	50.6 atmos.
2.	$-121.6^{\circ}$	50.6 "
3.	$-120.5^{\circ}$	50.6 "
4.	$-121.3^{\circ}$	50.6 "
5.	$-121.4^{\circ}$	50.6 "
6.	$-119.8^{\circ}$	50.6 "
7.	$-121.3^{\circ}$	50.6 "

In all seven determinations the critical pressure was found to be 50.6 atmospheres; but determinations of the critical temperature show slight differences. In experiments Nos. 3 and 6 less liquid argon was present in the tube than in the other five; in these the volume of liquid exceeded the volume of gas.

In determining the vapor pressures of argon, a tabular record of which is given below, I noticed slight differences of pressure according as I produced more or less of the liquid at the same temperature.

This proved that the sample of argon contained an inconsiderable admixture of another gas, more difficult to liquefy; it is doubtless the trace of nitrogen previously referred to. The mean of the seven estimations of the critical temperature is  $-121^{\circ}$ , and this may be taken as the critical temperature of argon.

At lower temperatures the following vapor pressures were recorded :

Expt.	Temperature.	Pressure.
8.	$-128.6^{\circ}$	38.0 atmos.
9.	$-129.6^{\circ}$	35.8 "
10.	$-129.4^{\circ}$	35.0 "
11.	$-129.3^{\circ}$	35.8 "
12.	$-129.6^{\circ}$	35.8 "
13.	$-134.4^{\circ}$	29.8 "
14.	$-135.1^{\circ}$	29.0 "
15.	$-136.2^{\circ}$	27.3 "
16.	$-138.3^{\circ}$	25.3 "
17.	$-139.1^{\circ}$	23.7 "

In Experiments Nos. 9, 10, and 17, the quantity of liquefied argon was very small, for it filled the tube only to a height of three to five mm., and in the other experiments the column of liquid argon was twenty mm. high or more.

*Determination of the Boiling and Freezing-Points.*

Two hundred cc. of liquid oxygen, prepared in my large apparatus,<sup>1</sup> was poured into a glass vessel with quadruple walls, so as to isolate the liquid from external heat. After the liquid oxygen had been thus poured under atmospheric pressure, a great part of it evaporated, but there still remained about seventy cc., boiling under atmospheric pressure. A calibrated tube, intended to receive the argon to be liquefied, and the hydrogen thermometer were immersed in the boiling oxygen. At this temperature ( $-182.7^{\circ}$ ) on admitting argon, no appearance of liquefaction could be noticed, even when compressed by adding a quarter of an atmosphere pressure to that of the atmosphere. This shows that its boiling-point lies below that of oxygen. But on diminishing the temperature of the liquid oxygen below  $-187^{\circ}$  the liquefaction of argon became manifest. When liquefaction had taken place I carefully equalized the pressure of the argon with that of the atmosphere, and regulated the temperature, so that the state of balance was maintained for a long time. This process gives the boiling-point of argon under atmospheric pressure. Four experiments gave the numbers  $-186.7^{\circ}$ ,  $-186.8^{\circ}$ ,  $-187.0^{\circ}$ , and  $-187.3^{\circ}$ . The mean is  $-186.9^{\circ}$ , which I consider to be the boiling-point under atmospheric pressure (740.5 mm.).

The quantity of argon used for these experiments, reduced to normal temperature and pressure was 95.5 cc.; the quantity of liquid corresponding to that volume of gas was approximately 0.114 cc. Hence the density of argon at its boiling-point may be taken as approximately 1.5. Two other determinations of the density of liquid argon, for which I employed still smaller quantities of the gas, yielded rather smaller numbers. Owing to the small amount of argon used for these experiments, the numbers given can not lay claim to great exactness; yet they prove that the density of liquid argon at its boiling-point ( $-187^{\circ}$ ) is much higher than that of oxygen, which I have found under similar conditions, to be 1.124.

By lowering the temperature of the oxygen to  $-191^{\circ}$  by slow exhaustion, the argon froze to a crystalline mass, resembling ice; on further lowering temperature it became white and opaque. When the temperature was raised it melted; four observations which I made to determine its melting-point gave the numbers:  $-189.0^{\circ}$ ,  $-190.6^{\circ}$ ,  $-189.6^{\circ}$ , and

<sup>1</sup> *Bulletin International de l'Academie de Cracovie*, June, 1890; also Wiedemann's *Bridgman*, 15, p. 29.

<sup>2</sup> I have redetermined the boiling-point of oxygen, using large quantities of oxygen, and a hydrogen thermometer of much larger dimensions than previously. The registered temperature is  $1.3^{\circ}$  lower than that which I previously recorded.

—189.4°. The mean of these numbers is —189.6°; and this may be accepted as the melting-point of argon.

In the table below I have given a comparison of physical constants, in which those of argon are compared with those of other so-called permanent gases. The data are from my previous work on the subject.

As can be seen from the appended table, argon belongs to the so-called "permanent" gases, and, as regards difficulty in liquefying it, it occupies the fourth place; *viz.*, between carbon monoxide and oxygen. Its behavior on liquefaction places it nearest to oxygen, but it differs entirely from oxygen in being solidifiable; as is well known, oxygen has not yet been made to assume a solid state.

Name.	Critical temperature.	Critical pressure.	Boiling-point.	Freezing-point.	Freezing pressure.	Density of gas.	Density of liquid at boiling-point.	Color of liquid
	Below.	Atmos.			mm.			
Hydrogen (H <sub>2</sub> ).....	—220.0°	20.0	?	?	?	1.0	?	Colorless
Nitrogen (N <sub>2</sub> )... ..	—146.0°	35.0	—194.4°	—214.0°	60	14.0	0.885	"
Carbonic oxide (CO)..	—139.5°	35.5	—190.0°	—207.0°	100	14.0	?	"
Argon (A <sub>1</sub> ).....	—121.0°	50.6	—187.0°	—189.6°	?	19.9	Abt. 1.5	"
Oxygen (O <sub>2</sub> ).....	—118.8°	50.8	—182.7°	?	?	16.0	1.124	Bluish.
Nitric oxide (NO).....	—93.5°	71.2	—153.6°	—167.0°	138	15.0	?	Colorless
Methane (CH <sub>4</sub> ).....	—81.8°	54.9	—164.0°	—185.8°	80	8.0	0.415	"

The high density of argon rendered it probable that its liquefaction would take place at a higher temperature than that at which oxygen liquefies. Its unexpectedly low critical temperature and boiling-point seem to have some relation to its unexpectedly simple molecular constitution.

Professor Ramsay exhibited two sealed glass tubes which, he said, contained argon, and handed them round. He said that he had been asked by some of his friends to show them the gas. It was, however, quite invisible.

The President (Lord Kelvin).—It will be a satisfaction, I am sure, to anyone present to have one of these tubes in his hand, and to have really handled a glass vessel containing argon.

Dr. Armstrong (President of the Chemical Society).—I am sure, sir, I can say at once that all present to-day who are able to judge of a communication of this kind, and all others outside, will gladly join in the chorus which Mr. Crookes has proposed should be sung. But I should like, speaking more on behalf of the chemists—and I am sure that Professor Ramsay will come over to me for the time and dissociate himself from his colleague—to say that we feel especially indebted on this occasion to Lord Rayleigh, not only on account of the extraordinarily important information which he has placed at our disposal, but more particularly on account of the example which he has set us. You, sir, **very**

fully alluded in your address this year to the patient manner in which Lord Rayleigh had tracked this new element to its home. I feel sure that the words which fell from you will meet with the warmest approbation everywhere where such work can be understood. (Applause.) The case contained in the paper is undoubtedly a very strong one. Of course, in the hurry of a meeting like this, it has not been so logically brought forward by the reader of the abstract as it might have been, in order to do it full justice; but yet I think it will be quite clear to all who have listened to him that there is a very strong body of evidence which makes it certain that there is in the atmosphere a constituent which has long been overlooked, and a constituent having most extraordinary properties. The paper is not one which, so far as the experimental facts are concerned, can be criticised here. No doubt it will meet with very considerable criticism throughout the world. People will not be satisfied to take all these statements for granted without checking them, and I have not the least doubt that very soon we shall have abundant confirmations of the correctness of the discovery. But, apart from the facts which are brought forward in this paper, there is a portion which is purely—one almost might say, if I may be allowed the expression on such an occasion—of a wildly speculative character; that is the portion dealing with the probable nature of this new element. Professor Ramsay, in his remarks, in a measure let the cat out of the bag in a way which is not apparent when you read the paper, because it is quite clear that, after all, the authors of this communication are not so entirely satisfied with the evidence to be adduced from the application of the Clausius method for the determination of the atomicity of the gas. I think that they have not sufficiently taken into account, in dealing with this evidence, the extraordinary property that this gas possesses. Nitrogen we know is a very inert form of matter, but we know that the character of nitrogen derived from its study in the atmosphere is of an altogether wrong character. We know perfectly well that, taken as an element and treated as an atom, nitrogen is probably one of the most active forms of matter known to us, and that the great difficulty we have in bringing about its association with fresh elements, when we deal with that gas, arises from its extreme activity—its extreme fondness for its own self. Now, if we can judge anything at all from the properties which we know belong to this new element, it is, I imagine, that it is like nitrogen, but “much more so.” It is quite conceivable that the condition which Professor Ramsay pointed out as being the only alternative to the one which is apparently accepted by the authors of the communication is a conceivable condition. It is quite likely that the two atoms exist so firmly locked in each other's embrace that there is no possibility for them to take notice of anything outside, and that they are perfectly content to roll on together without taking up any of the energy that is put into the molecule. There is a great deal to justify a view of this kind. Of course, it can not be discussed independently of what has been said with regard to the new gas

being a mixture; but it is quite clear that, as the discussion has gone on, the statements made in the paper are not so thoroughly accepted as one would think that they were. Mr. Crookes evidently wavers very much on this point with regard to there being two elements present, and I gather as much from Professor Ramsay's account. If we think that we are dealing with two gases here on the evidence of the spectroscope, there is no reason why we should not come to the same conclusion with regard to nitrogen and hydrogen. Oxygen, I believe, has three or four spectra, so that the spectroscopic evidence, after all, although it may be in a measure remarkable, does not appear to justify such a conclusion. The great difficulty that we have, I take it, in accepting the conclusion that we are dealing with an element having a molecular weight of forty, and an atomic weight of forty, arises from the difficulty of placing an element of that kind, which practically seems to me to have driven the authors to the conclusion that, possibly, they are dealing with a mixture. The difficulty would be got over, of course, if we were dealing with a complex body, and I think that was rather hinted at by Professor Ramsay when he referred to one of Olszewski's numbers. This low value, high as it is in comparison with that of nitrogen obtained from the density of the liquid, is a reason which would induce us to place it higher up in the scale of elements, and give it a lower weight. Of course, these are all matters which must be discussed later on more fully; they are matters which can only be discussed very gradually, as we learn more about this substance. As regards its inactivity, very possibly that may be exaggerated. It is very difficult, in a case like this, to find out what are the best conditions to make use of. We know perfectly well that, if we were not in possession of the electric spark, we could scarcely have discovered that nitrogen might be combined with hydrogen to form ammonia direct. We know that we can only bring about the combination of the two if we are in a position at once to remove the product; and that sort of thing may well obtain in a case like this. We know very well that there are comparatively few substances which can be directly associated with nitrogen. It is quite likely that here we are dealing with an element which has still fewer affinities, but it does not follow by any means yet—nor do the authors assert such to be the case—that we are dealing with an element which is entirely inactive even in the form in which it is presented to us. This is not the occasion to discuss the matter fully, but these are points which certainly<sup>9</sup> deserve consideration, and they are some of the first points which make this element of such importance and interest to us as chemists. In conclusion, I can only heartily congratulate the authors on having given us this communication.

Professor Rücker (President of the Physical Society).—I think it is very important on this occasion that we should remember that this is a discussion meeting of the Royal Society, a meeting held in this way for the first time, and a meeting at which reporters are present in order that the net result of the discussion shall go out at once to the world.\* It is, there-



fore, I think, extremely important that we should distinguish as clearly as possible between the various points of doubt which still may remain with regard to the new element which has been described to-day, and the one certain fact which comes out indisputably from the facts which have been laid before us; namely, that in spite of the doubt which may have existed on the matter for the last few weeks or months, we have it now beyond all question—and I quote the words of the President of the Chemical Society in saying so—that it is certain that we have here a new constituent of the atmosphere. What the importance of this is has already been mentioned, and I want once more to emphasize the fact that this central feature stands out quite clear, apart from whether we have one or two, and apart altogether from whether the various physical quantities which have been laid before us to-day have been measured with the accuracy which may be obtained in the future. But there is one particular point to which I should like to refer. It seems to me that one of the most interesting results arrived at from the physical point of view is the fact that the gas is monatomic. Some of us have had the opportunity of seeing the paper before it was read to-day, and we are therefore, perhaps, aware of one or two facts which, I think, were not actually mentioned by Professor Ramsay. One of these facts is that the experiments required to determine the ratio of the two specific heats were made twice over, or many times over, for all I know, but made in two different ways. They were made in a narrow tube, and they were made in a wide tube; and further check experiments were carried on in which other gases were compared with the new element. There can be no possibility of doubt as to a result of this sort when the experiments are carried out by two such men as Lord Rayleigh and Professor Ramsay. The matter is one which admits of no mistake when conducted in this way, and it must be accepted as certain that the element has that particular ratio of specific heats. Well, then the question arises, What follows from this? I think that it has not perhaps, been quite sufficiently pointed out that, in order that this ratio may be obtained if we are to use the ordinary mechanical theory of gases, it is necessary that the atom with which we are dealing should be regarded as spherical. Of course, I am well aware that our pictures of spherical and the like are, no doubt, only approximations to the truth; but if we are to conceive this atom as consisting of two which are closely united, the one with the other, we must nevertheless suppose, from that point of view, that they are so united as to form a sphere. That is only one way of putting it, but, nevertheless, it does create a difficulty which, I think, has not been altogether referred to before. I can only, in conclusion, say that, whatever the effect may be upon the great chemical generalization of Mendeleeff, that is, after all, an empirical law which is based, at present, upon no dynamical foundation. If it holds its own in this case, it will, of course, strengthen our belief in it, but, on the other hand, I do not think that it stands on the footing of those great

mechanical generalizations which could not be upset without upsetting the whole of our fundamental notions of science.

The President.—Among those present I am sure those who understand most of the subject will be anxious to speak. I now ask any person present to make remarks, and especially to ask questions.

Professor Roberts-Austen.—I should like to say that, when this beautiful discovery was communicated to the British Association, I ventured to point out that it was not too soon to consider its relation to the great metallurgical industries in which air is largely employed. In the Bessemer process alone you take some ten tons of iron and put it into a vessel called a converter. It is melted, and air is passed through to remove the carbon, silicon, phosphorus, and other impurities. That means that no less than 100,000 cubic feet of air pass through the metal. Therefore, 1,000 cubic feet of argon have gone somewhere. Now, I have taken Bessemer-blown metal, which has been treated with ferro-manganese, and have pumped out forty times its volume of gas, of which one-twentieth was nitrogen. In that nitrogen I have not been able to detect any argon that could not have come from the water which was necessarily used in the manipulation. I have taken a small quantity of air and abstracted argon from it, and obtained exactly the proportion that the authors say it contains, so I am perfectly certain that the manipulation is correct. But it remains to be seen whether the argon finds its way into the iron, as nitrogen undoubtedly does, and, if it does, whether it stays there, because there are certain peculiarities that make Bessemer metal different from other kinds of steel, and it would be most interesting if we could succeed in tracing it to some of this 1,000 cubic feet of argon which has either passed into the air or into the iron. I should just like to say that I could have wished that the authors of the paper had dialyzed the air through india-rubber, and not have merely used clay pipes. As one so long associated with Graham, I can only say how delighted he would have been had he known that his method would have been used by the authors of this paper, one of whom occupies Graham's own chair at University College.

Lord Rayleigh.—I have very little to add to the account which my colleague, Professor Ramsay, has given of this research. The research has been, in many respects, a very difficult one. I am not without experience of experimental difficulties, but certainly I have never encountered them in anything like so severe and aggravating a form as in this investigation. Every experiment that one attempts takes about ten days or a fortnight to carry out to any definite conclusion, and the result has been, of necessity, much less progress than we could have hoped for, and many of the questions have been left open which we could have wished to settle. One such question has just been alluded to by Professor Roberts-Austen; namely, the character of the gas transfused through india-rubber. That experiment has been upon our program, I may almost say from the first, but hitherto time has not been found to carry it out. The

difficulties of those parts of the research with which I have been more particularly connected have been very great. The preparation of the gas in sufficient quantity to experiment with at all has been no easy matter, and some of the results, such as those relating to the density of the gas, are consequently not so satisfactory and not so thoroughly elaborated as one could have wished. One point that has been mentioned relates to the argument in favor of the monatomicity of the gas. Of course, what is directly proved by the experiment, if it is good, is that the whole, or nearly the whole, of the energy put into the gas, when it is heated, is devoted to increasing the energy of its translatory motion, and that no margin remains over, as in the case of other gases, to be attributed to intermolecular or interatomic motion. At first sight it seems rather a strange thing that there should be no rotation in the molecules of the gas. How can it be? Can they be without rotation, or can the energy of their rotation be so small as to be negligible in comparison with the energy of the motion as a whole? That is a difficulty which I think has not been thoroughly met hitherto by the cultivators of the dynamical theory of gases; but apparently here we may accept it that no such energy exists, or that no such energy exists in any appreciable degree. Of course, that condition is quite well met by the suggestion which has been put forward, and which has also been communicated to us by Professor Fitzgerald, of Dublin, who writes as follows:

"The reason why the ratio of specific heats of 1.66 is supposed to prove monatomicity in a gas is because in a monatomic gas there are no internal motions of any consequence. Now, if the atoms in a molecule are so bound together that hardly any internal motions exist, it would, so far as specific heat is concerned, behave like a monatomic element. That the atoms in argon may be very closely connected seems likely from its very great chemical inertness. Hence, the conclusion from the ratio of its specific heats may be, not that it is monatomic, but that its atoms are so bound together in its molecule that the molecule behaves, as a whole, as if it were monatomic."

That argument is, no doubt, perfectly sound, but the difficulty remains how you can imagine two molecules joined together, which one figures roughly in the mind, and I suppose not wholly inaccurately, as somewhat like two spheres put together and touching one another—how it would be possible for such an excentrically-shaped atom as that to move about without acquiring a considerable energy of rotation. That is difficult, and I think the only interpretation is, that the gas is monatomic. No doubt the whole subject is one about which we know exceedingly little, mercury vapor being the only other gas at present which exhibits a similar property. I am not sure that any other point has been raised, but if any questions are asked, Professor Ramsay and myself are quite ready to give further explanations, so far as it is in our power to do so.

The President.—I wish to make a remark, not as from the chair, but with reference to the question which is now before us, as to the condition

under which the ratio of the specific heats could be exactly one and two-thirds. I do not admit that a spherical atom could fulfill that condition. A spherical atom would not be absolutely smooth. In other words, it must be a Boscovitch point. Neither can I admit that excessively rigid connection between two atoms could give it the quality of having no capacity whatever for a relative vibratory movement. It would need infinitely stiff connections to give it no capacity for relative vibratory movement; and if it had infinitely stiff relative connection the connection of the two bodies would be indissoluble, and they would remain one. In fact, I think that the only kind of atom that we can conceive as giving, in the dynamical theory of heat, rigorously the ratio of one and two-thirds for the specific heat is the ideal Boscovitch mathematical point endowed with the property of inertia, and with the other property of acting upon neighboring points with a force depending upon distance. I have now to ask for any further remarks. I do not wish to close this most interesting discussion. I hope we shall have further discussion and further questions.

If there are no more remarks and no questions to be put, I desire now, in the name of the Royal Society, to thank the Senate of the University of London for their hospitality on this occasion, a hospitality which I am sure we have all very much enjoyed. I have great pleasure in joining with the President of the Chemical Society, and the President of the Physical Society in congratulating Lord Rayleigh and Professor Ramsay on the brilliant success already obtained. (Great cheering.) I join with my brother Presidents in wishing them more and more success in the continuation of their work, and in thanking them heartily in the name of the Royal Society for the communication which they have given us this day. (Cheers.)

*Calcium Sulphite Stalactites and Stalagmites.*—Under a number of large wooden tanks, in which "Bisulphite of Lime," of the trade, has been stored for a year or more, a curious stalactitic formation was observed.

The "Bi-sulphite of Lime," seeping through minute openings in the bottoms of the tanks, had been precipitated as calcium sulphite by the evaporation of free sulphurous acid, in a manner perfectly analogous to the natural formation of stalactitic deposits of calcium carbonate.

The stalactites examined were from six to eighteen inches in length, generally with a small hole vertically through the center, granular in structure, more or less stained with iron, and partially oxidized to calcium sulphate. A few were made up of concentric rings of granular crystals, alternate rings being more deeply stained with iron. One specimen, radiately fibrous in

structure, was beautifully crystallized. The stalactites were usually irregular cones with the altitude from five to ten times the diameter of the base.

In many cases the stalactite and stalagmite had become united forming an irregular cylindrical column.

The stalagmites examined were all granular in structure and usually less deeply stained than the corresponding stalactites. One specimen was white and very well crystallized. Like the stalactites they were usually more or less oxidized. The vertical axis was shorter, in proportion to the diameter of the base, and the apex more rounded, than in case of the stalactites.

The phenomenon is deserving of attention as an illustration of the well-known analogy between the sulphites and carbonates of the alkaline earth metals, as regards insolubility in water, but ready solubility in water containing sulphurous or carbon dioxide respectively. It is also interesting as showing a further analogy between two classes of salts which do not fall in the same period in the Mendelejeff classification.

DAVID HANCOCK.

CUMBERLAND, MD., January 18, 1895.

---

### NEW BOOKS.

A TEXT-BOOK OF INORGANIC CHEMISTRY. DESCRIPTIVE, THEORETICAL, AND PRACTICAL. A MANUAL FOR ADVANCED STUDENTS. BY ALFRED A. BENNETT, PROFESSOR OF CHEMISTRY IN THE IOWA COLLEGE OF SCIENCE, AGRICULTURE, AND THE MECHANIC ARTS. 2 Vols., 12 mo. 11 Illustrations. New York, Boston, Chicago: Silver, Burdette & Co. 1892 and 1894. Introductory price, \$1.50 per volume.

It has lately been stated in a book review in these pages that there is doubtful room for new text-books on inorganic chemistry; and, in view of the important number of standard works of acknowledged value and usefulness extant, most instructors will heartily concur in this view. Every teacher, however, has his own ideas of how best to present the subject to his students to enable them to readily and intelligently grasp it, and whatever may be the text-book employed, it can in any case be followed only as a general guide and be adapted to the needs and conditions in each case. The work before us may fairly claim to be of such general adaptability as to be useful in most cases, and

particularly in those in which objective teaching, now properly so prevalent, has been adopted. It is essentially a laboratory guide rather than a lecture adjuvant, a manual rather than text-book, and its aim is to furnish such schemes for practical work with chemicals and apparatus in the hands of students as will lead them by actual practice and observation to grasp the fundamental principles of the science, describing the properties of the elements and compounds little further than is necessary to the development of these principles or to emphasize the facts that should be gleaned from observation and experiment.

The first volume (pp. 357) of the work is devoted to the so-called non-metallic elements, and after the usual brief discussion of matter and energy, the relations of physics and chemistry, and the conservation of matter and energy, begins with a study of hydrogen and the halogens and the combinations of the former with the latter. From the properties and reactions covered in this study are developed the hypotheses, theories, and laws which constitute, as it were, the axioms of chemistry. This general principle is followed throughout the work, and the facts concerning each element are studied in the following order: 1. Occurrence and distribution; 2. Methods of preparation; 3. Preparation; 4. Experimental study; 5. Physical properties; 6. Chemical properties; 7. Name, derivation, meaning, and symbol; 8. History; 9. Uses; 10. Special tests for recognition of the elements; 11. (For compounds.) The determination of molecular formulas. And along with this, theoretical considerations are developed in a logical manner.

Under the caption "Experimental Study" are offered directions for making experiments which, it is expected, will be explained to the class in the lecture room and will be carried out later in the laboratory by the students, who will likewise be required to keep copious notes of their operations and observations. Supplemental to these directions are offered certain arithmetical problems illustrative of the principle and properties developed, and unfinished equations which the student is directed to complete.

An interesting and novel feature of the book is the limited study of potassium and sodium in connection with, and imme-

diately following, that of the compounds of hydrogen, the halogens, and oxygen, thus "introduced in order that the learner may have some facts to use in the consideration of acids and bases."

The second volume (pp. 366) is devoted to the metallic elements, their properties, and reactions (pp. 299); the classification of the elements in accordance with the periodic law (pp. 18); a system of qualitative analysis, (pp. 47), concluding with a table of seventy-two elements with their atomic "masses," prepared by F. W. Clarke and a blank table of solubilities of salts to be filled by the student as he determines these properties in his experiments.

"Mass" is used in preference to weight and the system of spelling recommended by the committee of the American Association for the Advancement of Science followed throughout.

Having developed the significance of valence and atomic mass in the first volume, the author devotes considerable space in this volume, in connection with each metal, to the facts which determine its classification with regard to these properties; and in view of the difficulties which students frequently meet in acquiring familiarity with them, this provision will, in many cases, prove most valuable.

The volumes are, each of them, provided with excellently arranged indexes, are of such form and size as to be convenient for use either in the study, the lecture room, or the laboratory, and are offered in attractive style both as to binding and typography.

WM. MCMURTRIE.

QUALITATIVE CHEMICAL ANALYSIS OF INORGANIC SUBSTANCES AS PRACTICED IN GEORGETOWN COLLEGE, D. C. pp. 61. New York: American Book Company. 1894. Price \$1.50.

This small book is divided into four parts: I. Basic Analysis. II. Acid Analysis. III. Preliminary Examination. IV. Solution of Solid Substances.

The bases are grouped and numbered according to Fresenius. The method of describing the properties and characteristic reactions of the elements of each group is somewhat different from that commonly used. A brief note of the properties of the element itself is first given, then the names and formulas of the

most common soluble compounds, and then the insoluble compounds under which head the characteristic reactions are given by first naming the insoluble compound or precipitate and then stating how it is formed, giving its properties, etc. Although the author states that "only these facts have been selected which are indispensable in a course such as the one for which the book is intended," it would seem that too large a number of characteristic reactions are either omitted or reserved to the analytical tables and explanations of the tables, and that in consequence the student hardly did a sufficient number of these important experiments before going on with a group separation.

This form of arrangement, however, may possess some advantages over the usual method of procedure. Certain it is that the explanations connected with each table of analysis is one of the best features of the book and bears evidence of careful and conscientious work on the part of the author. In treating of the acids the usual preliminary experiments upon the characteristic reactions of the individual acids of each group are entirely dispensed with, and instead one passes immediately to their separation and detection. To be sure the special tests applied to the separate portions of the original solution are characteristic. And the explanation of them is apt, still here again it would seem that some experience should be had in noting their deportment toward certain reagents before going to their separation. The preliminary examination and the solution of substances is substantially the same as ordinarily given in most text-books.

W. J. KARSLAKE.

---

**ADDENDUM.**—Professor Mabery makes the following addition to his article in the February number, page 105, after the words "Morley determined with the utmost precision the proportions of oxygen without finding any appreciable variations," insert the following:

In certain conditions of the atmosphere, when a vertical descent of the upper portions occurs, Professor Morley observed a deficiency in oxygen equivalent to 0.16 per cent.



# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

---

### THE SUPERIORITY OF BARIUM HYDROXIDE SOLUTION AS AN ABSORBENT IN CARBON DETERMINA- TIONS IN STEEL.<sup>1</sup>

BY JAMES O. HANDY, Chemist of The Pittsburg Testing Laboratory, L't'd.

Received January 8, 1895.

THE use of barium hydroxide solution as an absorbent for carbon dioxide is not new. It has long been used for that purpose in air analysis. It has also been used to a very limited extent in carbon determinations in steel.

As an absorption apparatus, Geissler potash bulbs are compact and convenient; they can be used several times without refilling, and are therefore very widely employed. Their use is, however, accompanied by at least one disadvantage; *viz.*, the error caused by differences in the temperature or degree of moisture in the laboratory air at the beginning and end of a combustion. This error sometimes amounts to more than do the small quantities of carbon dioxide whose exact weight it is desired to ascertain. This fact is well known and the error is to a considerable extent eliminated by the following precautions:

(a) Take the last weight of the bulbs from one combustion as the initial weight for the next; if the bulbs have been freshly filled with potassium hydroxide, a blank combustion is always made before taking the weight of the bulbs.

(b) During combustions, keep the bulbs in a covered box and thus shield them as completely as possible from moisture, dust, and heat.

<sup>1</sup> Read at the Boston meeting, December 27, 1894.

(c) Weigh them always at the same interval after finishing the combustion.

In the Pittsburgh atmosphere, fog and smoke are often present. The changes in the degree of moisture are frequently very considerable, even in a few hours. Hence carbon determinations by potassium hydroxide bulbs are especially difficult.

When barium hydroxide solution is used as an absorbent for carbon dioxide it is possible to finish the analysis in at least three ways:

(1) The barium carbonate may be filtered off, washed, ignited, and weighed. This has been done successfully by Mr. Alex. G. McKenna, of Pittsburgh. He uses a special absorption apparatus to which the barium carbonate does not adhere.

(2) The excess of barium hydroxide solution may be titrated:

(a) By a standard oxalic acid without filtering off the barium carbonate, or (b) by standard sulphuric acid after filtering off the barium carbonate.

In either case phenolphthalein is the indicator which is used. I have found difficulty when using the oxalic acid titration in getting a satisfactory end point. With the sulphuric titration, no such trouble was experienced.

The facts that the ratios between C and  $\text{Ba}(\text{OH})_2$ ,  $\text{BaCO}_3$ , and  $\text{H}_2\text{SO}_4$ , are so much less than that of C to  $\text{CO}_2$ ,

$$\text{C} : \text{BaCO}_3 = 12 : 197.4 = 1 : 16 +$$

$$\text{C} : \text{Ba}(\text{OH})_2 = 12 : 171.4 = 1 : 14 +$$

$$\text{C} : \text{H}_2\text{SO}_4 = 12 : 98.0 = 1 : 8 +$$

$$\text{C} : \text{CO}_2 = 12 : 44.0 = 1 : 3 +$$

show the great advantage possessed by the barium hydroxide methods over the potassium hydroxide absorption for carbon dioxide.

When we consider also that the use of standard barium hydroxide and a titration method does away with the uncertain atmospheric moisture factor, it is at once plain that the method has several distinct points of superiority over the potassium hydroxide method.

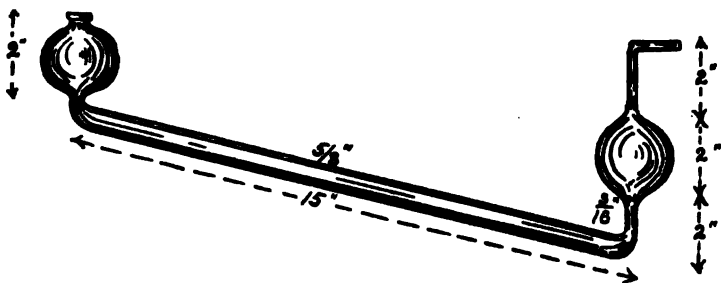
*Method for Steels of 0.06 to 0.20 per cent. carbon.*—Dissolve, by shaking in a glass-stoppered bottle, ten grams or more of 0.06 per cent. carbon steel or five grams of 0.20 per cent. steel in a mixture of copper and potassium chloride solution, one pound in

1,400 cc. of water, and hydrochloric acid. Use 600 cc. of the former and forty cc. of the latter for ten grams of steel and proportionately, more or less, for other amounts. Filter on asbestos which has been ignited in oxygen, wash as usual, and dry the carbon residue at  $100^{\circ}$  C. Transfer to combustion tube and make combustion as usual. Regulate the oxygen current so that one bubble starts up the absorption tube just as its predecessor reaches the top.

Between the combustion tube and the absorption apparatus I place only a U tube containing calcium chloride in the first limb and anhydrous copper sulphate in the other.

The absorption apparatus consists of two glass tubes like the one shown in the sketch.

Each tube contains fifty cc. of barium hydroxide solution. Tubes of this shape seem to give the bubbles of gas a rapid rotating motion as they rise through the barium hydroxide solution. As a result, the absorption is very perfect. This is an important point. Many forms of apparatus fail utterly in this particular.



When the combustion is complete and pure air or oxygen has been passed long enough to expel all carbon dioxide, the absorption apparatus is disconnected and the contents filtered.

During the filtration, air purified by bubbling through potassium hydroxide solution is kept playing on the surface of the barium hydroxide solution. This prevents the formation of barium carbonate by the action of atmospheric carbon dioxide on the excess of barium hydroxide. Since laboratory air is often very impure, this precaution is imperative.

## 250 SUPERIORITY OF BARIUM HYDROXIDE SOLUTION, ETC.

The barium carbonate precipitate is washed with distilled water which is free from carbon dioxide. That which has been freshly distilled is best. The water from wash-bottles or flasks is unavailable. When kept in a stock carboy, connected with the laboratory still, I have always found my distilled water free from carbon dioxide. The excess of barium hydroxide solution is quickly titrated after filtering off the barium carbonate and washing it with water free from carbon dioxide.

Standard sulphuric acid is used, with phenolphthalein as indicator. Certain precautions are necessary when filling the absorption tubes with barium hydroxide solution.

By connecting a potassium hydroxide wash-bottle and calcium chloride tube with the blast-pipe, pure air can be easily obtained.

Force pure air through the absorption tubes for ten minutes; then close them by rubber connections. While drawing up the fifty cc. of barium hydroxide solution have the pure air current passing into the barium hydroxide bottle. When ready, allow the barium hydroxide solution to run into the absorption tube closing the same again and keeping so until ready to connect with the combustion train.

### EXPERIMENTS.

	KOH Method Chemist "L" "C"	Ba(OH) <sub>2</sub> method Chemist "H"	Color test KOH standard.
Steel "A" Carbon	0.14	0.134	0.14
" 11834.7 "	....	0.109	0.11
" 11857.0 "	0.17	0.178	0.17
" "M" "	0.08%	{ 0.090    0.093 0.091 and 0.092 }	0.08

### STANDARD SOLUTIONS.

*Standard Barium Hydroxide Solution.*—Twenty grams of barium hydroxide are dissolved in water in a stoppered graduate and then made up to one liter. Filter into a bottle containing pure air, (air which has passed through the potassium hydroxide wash-bottle). Keep a current of pure air playing on the surface of the solution during filtration. It will then remain clear and bright even if the laboratory air is quite impure. Of this solution fifty cc. are more than sufficient for the carbon from five grams of two-tenths per cent. carbon steel. A second absorption tube is usually kept in the train but is rarely necessary.

*Standard Sulphuric Acid.*—A decinormal solution is used. Of this one cc. = 0.0006 gram carbon.

This method is best adapted for low carbon steels, because only small quantities of barium carbonate have to be filtered and washed.

When analyzing high carbon steels I have used smaller weights of steel (one or two grams) and have rinsed the barium carbonate and excess of barium hydroxide solution into a liter flask; after making up to one liter with pure water, I filter off 200 cc. and titrate by standard sulphuric acid. Steel 11920 gave 1.35 per cent. and 1.35. per cent. carbon by this method.

The work which I have been able to do seems to me to suffice to call attention to the merits of the barium hydroxide methods.

## THE CONTRIBUTIONS OF CHEMISTRY TO THE METHODS OF PREVENTING AND EXTINGUISHING CONFLAGRATION.

BY THOMAS H. NORTON.

[Continued from page 147.]

The interaction involved the formation of gypsum and aluminum chloride, which, in turn, precipitated the gelatin and converted it into a leatherlike insoluble substance. The object was to fill the pores of the fabric with gypsum and cover the surface with a hard binding material. Sir Frederick Abel, in reporting on the feasibility of this process found that it rendered the canvas very difficult of ignition, but that it also gave to it a degree of rigidity and harshness which forbade its use. In 1856 Maugham<sup>1</sup> patented the use of ammonium phosphate and starch; and in 1857 Thouret<sup>1</sup> patented the use of a mixture of three parts of ammonium chloride and two parts of ammonium phosphate, adopting these proportions on account of cheapness, although the ammonium phosphate alone gave most excellent results.

During this period the importance of better protection for the scenery of theaters was recognized. After a serious fire in the Berlin opera house, the custom was inaugurated of soaking all scenery in a strong alum solution.<sup>2</sup> In 1857 a commission in

<sup>1</sup> Amer. Arch., 13 and 14.

<sup>2</sup> Frémy, *Dict. de Chimie*, 10.

Paris carefully examined the subject, and in accordance with their recommendations the order was issued to have all scenery in theaters impregnated with waterglass.<sup>1</sup> After the lapse of some years it was found that scenery thus treated possessed but slight resistant power. The explanation advanced is that the waterglass, on drying, contracts steadily until the solid particles finally sit very lightly on the yarn of the canvas. Another is that a solvent action is exercised by the water in the water-colors often used by scenic artists. It has been suggested by Hexamer that the impregnation with waterglass could be advantageously followed by treatment with hydrochloric acid, thus precipitating silicic acid directly in the fibers of the yarn, a process practically similar to that of the use of mordants in dyeing.

Versmann and Oppenheim,<sup>2</sup> in 1859, reported to the British Association for the Advancement of Science the results of an elaborate and extended study on the use of salts in treating fabrics, including some forty different substances in the range of their experimentation. Their tests were made on muslin free from starch, weighing 33.4 grams to twelve square inches; and more in the direction of ascertaining the strength of the most effective solution, rather than the weight of a given salt absorbed. After immersion in a solution the excess was removed by pressing and not by wringing. Tests were conducted on a large scale in muslin works and laundries. None of the salts recommended to that time were found available where the operation of ironing was to be performed. Either a smooth surface could not be obtained, or the material was injured on the application of heat.

The valuable results of Versmann and Oppenheim may be briefly summarized as follows:

KCN—very effective in a ten per cent. solution, but poisonous and expensive.

$\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ —both very effective in a ten per cent. solution, but the one is efflorescent and the other deliquescent.

$\text{NaHCCO}_3$ —very effective in a six per cent. solution, but carbon dioxide is rapidly lost and the protective power disappears.

<sup>1</sup> Frémy, *Dict. de Chimie*, 10.

<sup>2</sup> Loc. cit.

$\text{Na}_2\text{B}_4\text{O}_{10}$ ,—very effective, but on warming, boric acid is liberated and attacks the fabric.

$\text{NaOH}$ ,—effective in eight per cent. solution.

$\text{Na}_2\text{SO}_4$ ,—no effect.

$\text{NaHSO}_4$ ,—twenty per cent. solution is protective, but the stuff is gradually attacked.

$\text{Na}_2\text{SO}_3$ ,—twenty-five per cent. solution is protective, but the stuff is gradually attacked.

$\text{Na}_2\text{HPO}_4$ ,—a saturated solution is effective, but the fabric becomes perfectly stiff.

$\text{Na}_2\text{SiO}_3$ ,—the fabric is strongly attacked and the appearance affected.

$\text{Na}_2\text{SnO}_3$ ,—protective, but attacks the fabric.

$(\text{NH}_4)_2\text{CO}_3$ ,—too volatile.

$(\text{NH}_4)_2\text{C}_2\text{O}_4$ ,—renders the fabric combustible.

$(\text{NH}_4)_2\text{B}_4\text{O}_{10}$ ,—a five per cent. solution gives good protection, but the acid is easily liberated and corrodes.

$(\text{NH}_4)_2\text{SO}_4$ ,—a ten per cent. solution is very effective, but the salt is deliquescent.

$\text{NH}_4\text{Cl}$ ,—a twenty-five per cent. solution gives excellent results, but stiffens the fabric.

$(\text{NH}_4)_2\text{HPO}_4$ ,—gives excellent results alone or when mixed with ammonium chloride as in Thouret's patent. Maugham's mixture of this salt with starch was not available on account of uneven distribution throughout the mass.

$(\text{NH}_4)_2\text{SO}_4$ ,—when rendered perfectly neutral by a little ammonium carbonate, this yields the best results of all the ammonium salts. Chevalier's mixture of this salt and borax attacks fabrics at a summer temperature.

$\text{SnCl}_2$ $\text{SnCl}_4$ $\text{SrCl}_2 \cdot 2\text{NH}_4\text{Cl}$	$\left. \begin{array}{l} \\ \\ \end{array} \right\}$	All these are good protectives, but attack the material.
---	--	--

The following salts give good protection when used in solutions of the strength indicated, but are not available on account of price, or corrosive, or other properties;  $\text{BaCl}_2$ , fifty per cent. solution,  $\text{CaCl}_2$ , ten per cent.,  $\text{Al}_2(\text{SO}_4)_3$ , seventy-seven per cent.,  $\text{KAl}_2(\text{SO}_4)_4$ , thirty-three per cent.,  $\text{NH}_4\text{Al}_2(\text{SO}_4)_4$ , twenty-five per cent.,  $\text{FeSO}_4$ , fifty-three per cent.,  $\text{CuSO}_4$ , eighteen per cent.,  $\text{ZnSO}_4$ , twenty per cent., and  $\text{ZnCl}_2$ , eight per cent.

Unsuccessful attempts were made to fix upon the fibers such protective salts as  $\text{BaSO}_4$ ,  $\text{Al}_2(\text{PO}_4)_3$ , and various silicates. Zinc oxide and aluminum oxide gave good results, but would not adhere when washed. Antimony chloride was effective and withstood water, but not soap or soda. Stannous borate, phosphate, and arsenate gave good protection and withstood washing, but gave a yellow tinge to the fabric. Zinc and calcium stannates, while efficient protectors, would not withstand soap or soda. Stannic oxide was fixed permanently but imparted a yellow color. It seemed to be well adapted for coarse material, sail-cloth, canvas, etc.

For light stuffs, to be ironed, sodium tungstate was found to be the best agent, and the most effective solution is one of 28° Tw. or 1.14 sp. gr., containing also about three per cent. of sodium phosphate in order to prevent the formation and precipitation of the acid tungstate.

Where the hot iron is not to be applied directly, ammonium sulphate can be advantageously employed in a ten per cent. solution. The fabric is to be dried in chambers; the ordinary colors on prints, except madder purple, are unaffected.

Versmann and Oppenheim at first sought to produce, artificially, conditions similar to those existing in animal fibers such as silk and wool, which are not inflammable, and which contain about eighteen per cent. of nitrogen. Experiments to incorporate nitrogenous substances such as glue or albumen into vegetable fiber were without practical result, although it was found possible by the use of urea to introduce into muslin thirteen per cent. of nitrogen, rendering it thereby uninflammable.

Essentially the same object is obtained, as we have seen, by the use of ammoniacal salts.

Sir Frederick Abel<sup>1</sup> made reports in 1859 and 1860 to the English Ordnance Department on Versmann and Oppenheim's results, especially with reference to the protection of canvas. The advantages of sodium tungstate for light fabrics were fully confirmed by him. The availability of stannic oxide for sail-cloth was likewise confirmed. Sail-cloth was most effectively deprived of its inflammability thereby, and the protective agent was permanently fixed in the fabric, being affected neither by friction nor

<sup>1</sup> Amer. Arch., 13 and 14.



by repeated washing, while the strength of the canvas was not diminished. The only objections to the use of stannic oxide were: First, the notable increase in weight amounting to fifty per cent. of the original weight of the canvas; and, second, the comparative costliness. While the first objection was regarded by Abel as practically inseparable from the permanent fireproofing of fabrics, the second he considered much more serious. Accordingly, we find him, shortly after, patenting and submitting to the Ordnance Department, a cheaper process for fireproofing canvas, consisting of the deposition in the fiber of a double sodium and lead silicate. Boiling solutions of basic lead acetate and of waterglass were used. I have not been able to ascertain how extended a use was made of this process. Abel in his reports states that he finds saturation with a solution of waterglass alone an efficient protective; but that its value is temporary only. He sums up the difficulties to be encountered in fireproofing fabrics as follows:

(1) The protective material renders the fabric harsh and rigid; or (2) it absorbs moisture and keeps the fabric damp; or (3) it affects the strength and durability of the fabric; or (4) it is easily detached by rubbing or shaking; or (5) it is soluble in water and must be renewed after wetting.

In 1870 Abel<sup>1</sup> recommended to the Ordnance Department treatment with calcium chloride for rope mantelets on board warships in order to keep them damp and prevent ignition during the firing of guns.

In 1871 the Austrian chemist Patera<sup>2</sup> introduced the use of magnesium borate as a protective for fine fabrics and delicate colors. The materials are soaked in a bath of three parts of borax and two and one-half parts of magnesium sulphate in twenty parts of water with the necessary amount of starch, then wrung between cloths and dried. For coarser stuffs he found mixtures of ammonium sulphate and gypsum effective.

In 1882 a special committee of the Franklin Institute of Philadelphia reporting on safety devices for theaters, gave the results of their experiments on the fireproofing of scenery and gauze.<sup>1</sup> They obtained the best results with the material devised by Dr.

<sup>1</sup> Amer. Arch., 13 and 14.

<sup>2</sup> Flammenschutzmittel, Wien, 1871.

J. Papen, of Frankfort, Germany. The details of its composition are not given, but it has rendered excellent results in the Frankfort opera house, yielding efficient protection, not altering in time, nor affecting the strength or color of the fabrics, and producing no injurious effect on the voices of singers or actors. The committee obtained also very good results from the use of ammonium sulphate, of silica precipitated on the fiber, and from the processes of Gantsch and Judlin, details of which are also lacking.<sup>1</sup>

This question of fireproofing scenery, etc., in theaters had already been the subject of considerable investigation. In 1877 a committee of the House of Commons took evidence on the matter, and we find Mr. Henderson, of the Criterion theater testifying that he used regularly sodium tungstate in the preparation of new scenery; although it was not available for old scenery.

A committee of the London Society of Arts,<sup>1</sup> in 1883, made a report on the same subject, recommending sodium tungstate as the best safeguard for scenery. They found on investigation, that the scenery in nearly all London theaters was treated with some fire-proof preparation; most having as a basis a borate or a silicate. They add in their report: "these compositions do not prevent the evolution of gas when an article is exposed to sufficient heat; and the gas takes fire and burns. When the external source of heat is removed, no more gas is evolved, and combustion ceases. Prepared articles burn when exposed to sufficient heat, but do not support combustion. One effect of this is that it is very much more difficult to set such materials on fire; and this either prevents the breaking out of the fire, or renders it much more easy to deal with when broken out."

The theaters of Paris had already used largely for protecting scenery, a solution of the following composition devised by Martin and Tessier:<sup>2</sup>

Ammonium sulphate.....	8
Ammonium carbonate.....	2
Boric acid.....	3
Borax.....	1
Starch .....	2
Water.....	100

<sup>1</sup> Amer. Arch, 23 and 24.    <sup>2</sup> Frémy, *Dict. de Chimie*, 10.

Among recently introduced preparations for the purpose in view, the efficacy of which has not been fully tested, are the following:

Vendt and Herard,<sup>1</sup> 1885. A solution of eight parts ammonium chloride, ten parts ammonium sulphate, two and one-quarter parts sodium thiosulphate, four and one-half parts borax, and seventy-two parts water.

Winckelman : <sup>2</sup> —Manganese chloride.....	33 parts.
Glacial phosphoric acid...	20 "
Borax.....	10 "
Magnesium chloride.....	12 "
Magnesium sulphate.....	25 "

Fabrics are boiled for six hours in this solution and become thoroughly impregnated with insoluble double salts.

Martin and Tessier : <sup>2</sup> —Boric acid.....	6 parts.
Borax.....	3 "
Ammonium chloride.	15 "
Water .....	100 "

Used chiefly for cordage, sail-cloth, canvas, and straw, the materials being steeped in the solution.

Vogt : <sup>2</sup> —Ammonium chloride.....	2 parts.
Zinc sulphate.....	1 "
Water.....	20 "

Starch as needed.

Subrath : <sup>2</sup> —Alum.....	5 "
Ammonium phosphate.....	5 "
Water .....	90 "

Hattin :<sup>2</sup>—Calcium dihydrogen phosphate, ammonia, and gelatinous silica.

Pereles :<sup>2</sup>—Combined solutions of sodium phosphate, silicate, and tungstate.

Nicoll :<sup>2</sup>—Solution of alum, borax, sodium tungstate, and dextrin, or equal weights of calcium acetate and chloride in hot water.

These comprise the processes for the protection of fabrics introduced up to the present time. As is easily seen, the use of sodium tungstate, the borates, or ammonium salts alone or in mixtures is the striking feature.

<sup>1</sup> *Génie civ.*, 6, 227.

<sup>2</sup> *Sc. Amer. Cyclop. of Receipts*, p. 217.

A few words with regard to the methods of manufacturing or protecting paper are here in place.

Martin and Tessier<sup>1</sup> used the following bath for paper whether printed or unprinted.

Ammonium sulphate...	8	parts.
Boric acid.....	3	"
Borax.....	1.7	"
Water.....	100	"

The solution is placed in a vat, at the end of the paper-making machine and kept at 50° C.

Paper thus treated is non-inflammable. The value in many kinds of business of a totally incombustible paper is easily appreciated; and several varieties, all based on a large use of asbestos, are in vogue. L. Frobeen's paper is made from ninety-five per cent. of asbestos and five per cent. of wood-pulp mixed in water containing borax and glue. For ink he uses a mixture of platinum chloride and india ink.

Halfpennig's paper<sup>1</sup> is made from one part vegetable fiber, two parts asbestos, one-tenth part borax, and one-fifth part alum, formed in the ordinary way into a pulp to which waterglass is sometimes added. A paper of great flexibility and strength is obtained by coating sheets of linen on both sides with the incombustible paper. His ink is a mixture of graphite, copal, copperas, and indigo sulphate.

Paper is also made from pure asbestos and from asbestos mixed with alum, aluminum sulphate, zinc chloride, and resin soap.

A fire-proof writing-ink is an ammoniacal solution of silver nitrate, with a little india-ink, while platinum chloride mixed with lamp-black and varnish is employed as a fire-proof printing-ink.<sup>1</sup>

#### METHODS FOR RENDERING WOOD INFLAMMABLE.

In taking up next, the history of the efforts to render wood non-inflammable we encounter two distinct methods of procedure. The first is impregnation by the solutions of the chemical compounds which are to be operative, and includes such variations as the precipitation of insoluble salts within the wood by double

<sup>1</sup> Sc. Amer. Cyclop. of Receipts, p. 217.

decomposition; the second is the covering of the exterior of wood by protective coatings. In the case of existing structures, the latter is evidently the only means available.

The first recorded effort to protect wood was made at Munich in 1823, during the rebuilding of the Royal opera house after destruction by fire.<sup>1</sup> On the recommendation of Professor Fuchs all of the woodwork then received several coatings of waterglass. The surface covered was 400,000 square feet, and the cost was \$1,000, or at the rate of \$1 for 400 feet. Professor Fuchs prepared his solution by treating ten parts of caustic alkali, fifteen parts of infusorial earth, and one part of charcoal, with water. A somewhat similar composition was also in vogue then in England. It was made by grinding in oil one part of fine sand, two parts of wood-ashes, and three parts of slaked lime, and was applied with a brush. Fuchs' protective kept well, and was regarded as effective for twenty years, but later tests showed that its chemical composition was materially changed, and it no longer afforded security. It may be mentioned here that it was not then found available for scenery on account of the gloss it imparted. During this period the following mixtures came into vogue, chiefly for external protection, as in the case of shingled roofs: three parts of wood-ashes and one part of boiled linseed-oil; three parts of alum and one part of copperas; ashes and lime with skimmed milk as a binding material.

In 1841 Payne<sup>2</sup> introduced his combined process for rendering wood not only unflammable, but also proof against wet and dry rot and insects. It consisted in the precipitation throughout the mass of a piece of timber, of barium or calcium sulphate by double decomposition. In carrying out the process, wood is introduced into a capacious cylinder, the air is drawn out by steam, and a solution of barium or calcium sulphide is injected into the partial vacuum; the cylinder is exhausted again and then completely filled with the solution of the sulphide; pressure is increased to 140 pounds per square inch, and after an hour the solution is drawn off. The operation is then repeated, use being made of a solution of copperas; as a result the pores of the wood are largely

<sup>1</sup> Rymer-Jones, *Ecl. Eng. Mag.*, 33, 55, 1885; Hexamer, *Jour. of the Frank. Inst.*, 114, 125.

<sup>2</sup> Rymer-Jones, *Ecl. Eng. Mag.*, 33, 55, 1885.

filled with the insoluble sulphate and it becomes hard as stone. The soft, porous, cheaper grades of wood are thus rendered equal in point of durability and strength to the hardest varieties of timber. Wood prepared in this way is largely used in England in connection with public works and railways.

[TO BE CONTINUED.]

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY U. S. DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY, No. 12.]

## NOTE ON THE ESTIMATION OF IRON AND ALUMINA IN PHOSPHATES.<sup>1</sup>

By K. P. MCELROY.

Received January 2, 1895.

**I**N 1888 Dr. Crampton, then First Assistant Chemist of the United States Department of Agriculture, was engaged in the analysis of a lot of baking-powders and did me the honor to entrust to me a portion of the analytical work. Among other things I had to determine the alumina in a number of alum phosphate powders and met with the usual difficulties. By the method I was instructed to use, I found it impossible to get results that were concordant. I therefore systematically went through all the known methods for separating alumina from phosphoric acid and finally decided to use the one accredited to Mr. T. R. Ogilvie in Crookes' Select Methods (page 538, edition of 1886). Briefly stated the method consists in neutralizing the filtrate from the phosphomolybdate precipitate with ammonia, redissolving the precipitate of mixed sesquioxides thus formed, in nitric acid, once more precipitating, filtering, burning, and weighing. The process gave very good duplicate results, and a trial with a known amount of alumina in the form of alum mixed with sodium phosphate gave results sufficiently near theory. This, together with the fact of its having appeared in a work so standard as that of Crookes, seemed sufficient credentials for the method, and I placidly went ahead with its use. When Dr. Crampton prepared his manuscript (which I did not see prior to publication) for his bulletin on baking-powders (Bulletin 13, Part Five, Division of Chemistry, U. S. Department of Agriculture) he gave me credit for the minor modifications I had made

<sup>1</sup> Read at the Boston Meeting, December 27, 1894.

in the method, such as getting the alumina into solution, making up to volume, and the like. As to the main part of the method, the precipitation of alumina by ammonia in presence of molybdate solution, he had as little intention of accrediting it to me as I had of claiming it. He simply said (page 595) that the method "was adapted to the powders by Mr. K. P. McElroy."

Several years later Mr. W. H. Krug of this laboratory was engaged in making an exhaustive examination of a number of phosphate samples and had considerable trouble in determining iron and aluminum. In this connection he tried a number of the current methods on synthetic solutions and got results not agreeing with each other or with theory. At this juncture I suggested that he try the molybdate method. He used it on some phosphates which he had previously examined by the Glaser, Stutzer, etc., methods and obtained much better results. Subsequently he published a paper (*J. Anal. Appl. Chem.*, 1891, 5, 671) detailing his work and incidentally he courteously acknowledged my suggestion by saying of the molybdate method that it "was first used in this laboratory by Mr. K. P. McElroy for the estimation of alumina in phosphatic baking-powders." I had also suggested to Mr. Krug some modifications differing in minor detail from those of Ogilvie, by which it would be possible to determine calcium and magnesium in the same portion after precipitation of the iron and aluminum, and these Mr. Krug also published giving me full credit.

For some time since I have known that various chemists had fallen into the habit of calling this method for ferric oxide alumina, the "McElroy method" or "Krug method." Neither of us has taken the trouble to correct this mistake except orally since Crookes' *Select Methods* is a book of nearly as frequent occurrence in chemical laboratories as Fresenius' *Quantitative Analysis*, and publishing such a denial of authorship seemed nearly as ridiculous as it would be for one of us to rush into print to announce that he was not the originator of the method for the estimation of sulphuric acid as barium sulphate. Recently, however, a Northern chemist wrote a letter to the Department of Agriculture, designating the method by my name and announcing that in the case of a certain phosphate rock the method had

failed to give results concordant with those of other chemists using other methods. I had always known that the molybdate method did not give results agreeing very closely with those of other methods, but as I had also known that most of these other methods gave incorrect results, I had not laid the fact up against the molybdate method. In view of this specific complaint, however, I have tried the method on known solutions and am astonished to find that it really is liable to lead to grave error.

In this work I tried several samples of the molybdate solutions prepared according to the directions of the Association of Official Agricultural Chemists, which happened to be in the laboratory and found that they gave varying results. The worst results were obtained with a solution made up about six months ago, from which a heavy crystallization has taken place, leaving the residual liquid so weak that it requires over 100 cc. to precipitate the amount of phosphoric acid supposed to be thrown down by fifty cc. of a fresh solution. In two beakers I placed portions of ferrous sulphate representing each 56.4 mgms. of ferric oxide, added a solution of sodium phosphate representing 100 mgms. of phosphorus pentoxide to each, brought into solution in weak nitric acid, oxidized with bromine water, and then precipitated with the molybdate. I washed the precipitate with weak nitric acid and neutralized the combined filtrate and washings with ammonia. The resultant precipitate was dissolved in a solution of ammonium nitrate and nitric acid, filtered, and again thrown down. This precipitate was collected on a filter, burnt, and weighed. The amount recovered was respectively 56.9 and 57.3 mgms., showing a small plus error. In a duplicate set of experiments calcium nitrate equivalent to 400 mgms. of calcium oxide was added to each of the initial solutions. The amount of precipitate recovered in one case was 62.3 mgms. and in another 63.1 mgms., showing a large plus error. During the first precipitation a heavy white crystalline deposit of calcium molybdate occurred. The weighed precipitate was found to contain both lime and molybdic acid, showing that the same phenomenon had occurred in the second precipitation, though it was not visible to the eye.

In each of two beakers were next placed 35.6 mgms. of



alumina in the form of ammonia alum, together with 100 mgms. of phosphorus pentoxide in the form of sodium phosphate and the mixture treated as were those containing iron. The two precipitates of aluminum oxide finally obtained, weighed respectively 28.9 and 29.3 mgms., showing a large minus error. Another set containing 400 mgms. of lime was run through. The same precipitation of calcium molybdate was found to occur. The weights of alumina obtained were but 19.8 and 20.6 mgms. respectively, showing a much larger minus error.

From the above surprisingly bad results it is shown conclusively that the molybdate method for iron oxide and alumina, at least in this form is not at all trustworthy. Yet I have myself at times, and so have others, obtained good results by its use where these results were checked against those made by some of the standard methods used in delicate work.

### SOME PRACTICAL POINTS IN THE MANUFACTURE OF NITROGLYCEROL.<sup>1</sup>

BY J. E. BLOMEN, PH.D.

Received January 2, 1895.

FROM the very beginning of the commercial manufacture of nitroglycerol the aim of the inventors and manufacturers has been to eliminate the dangers of the operation to the highest possible extent and they have been so successful in this that very few, if any of the many accidents on record can be traced back to the apparatus. The problem is simple enough as the reaction is easily controlled. The indications of approaching danger are clear and the means to avoid it are easily kept at hand. From the old wooden boxes worked by hand with a paddle-wheel to the present elaborate apparatus, the principle is the same—to secure an even and low temperature through the mass of the mixture of acids and nitroglycerol.

It has long been considered that the safest way of stirring is with compressed air, but this can hardly be taken as an axiom. The water, which is formed during the reaction, is of the same temperature as the mixture and does not tend to elevate the temperature, but the moisture brought in with the air certainly does

<sup>1</sup> Read at the Boston Meeting, December 27, 1894.

raise the temperature as soon as it comes in contact with the acid. To prove this point air of the temperature of  $82^{\circ}\text{F.}$  was passed for five hours through a mixture of nitroglycerol acids (three-fifths sulphuric acid to two-fifths nitric acid) of  $86^{\circ}$  for five hours. After thirty minutes the temperature had risen to  $92^{\circ}$ , after one hour to  $93\frac{1}{2}^{\circ}$ , after two hours to  $94^{\circ}$ , after three hours to  $94\frac{3}{4}^{\circ}$ , after four hours to  $95\frac{1}{2}^{\circ}$ , and after five hours to  $95\frac{3}{4}^{\circ}$ , the temperature of the air remaining constant and the barometric pressure being 762 mm. during the entire experiment.

The apparatus is necessarily far away from the air-compressor and the air therefor has to be carried in pipes for a considerable distance. If then, as frequently happens, the moisture of the air (when not used for stirring) is condensed a considerable quantity of water is forced into the said mixture at one time and it becomes difficult to control the apparatus. Besides a stoppage in the pipe-line may take place at any time—for instance from a bad leakage, from an ice-plug or other substances in a pipe-section, or something may suddenly happen to the air-compressor. For these reasons it is doubtful if this system has any advantage over a stirrer or serpentine screw operated by an engine close at hand and which can be supervised by the operator. The latter way is besides decidedly the more economical as the moisture in the air (most of which comes in at the beginning of the operation) tends to dilute the acid mixture at the time when it is most important that the latter should be as strong as possible and the continuous forcing of warm air through nitric acid cannot but weaken this to a considerable extent.

It is true that when air is used the cooling surface can be better distributed by means of a number of smaller coils through the whole apparatus, but quite sufficient cooling surface is obtained by one big coil (embracing the serpentine screw or paddle-stirrer) when the mixture of the nitroglycerol acids is continually thrown against this and the sides of the apparatus cooled off by a water-jacket.

The question of how big a charge should be used at one time has been a matter of considerable controversy between expert nitroglycerol manufacturers. Of course it would be of the greatest advantage and convenience to use an apparatus big enough

to make one day's output of nitroglycerol in one operation, but this is hardly practical. It seems to be the experience of manufacturing chemists that very few chemical reactions can be effected with advantage on a very large scale; the nearer the operations come to the laboratory conditions the better is the result. This maxim is particularly true in this case. The dilution of the acids by the water formed is considerable— $\text{C}_2\text{H}_5\text{—O}_2\text{H}_2 + 3(\text{H—O—NO}_2) = \text{C}_2\text{H}_5\text{—O}_2\text{—(NO}_2)_3 + 3\text{H}_2\text{O}$ —and the acid mixture is consequently rapidly weakened. This cannot but have a serious effect on the reaction and if a very big charge is operated the acid mixture necessarily becomes uneconomical in composition. If air is used for stirring, of course, that will also weaken the mixture the longer it is used. Furthermore the acids will always find some little nook or corner of the apparatus—be this of lead or iron—that is weak and in a short time it will act upon it so that the apparatus must be repaired or renewed, and if it then is very big, the trouble and cost this will cause is obvious. Besides, if a charge should need to be drowned, as will happen, the loss is heavy.

On the other hand a charge should not be made too small, because it would take too much time and labor to cool off the acid mixture and rearrange the operation. A convenient charge to operate is one that will take one drum of the acid at a time. One drum holds about (or can by contract be made to hold exactly) 1,500 pounds of mixed acids. Experience has shown that the best composition of acids is three-fifths of the strongest sulphuric acid to two-fifths of the strongest possible nitric acid and 1,500 pounds of this mixture will nearly fill an ordinary iron drum. It has further been proved that it takes a little more than seven pounds of this mixture to each pound of glycerol to obtain a good yield of nitroglycerol. If therefore the apparatus is constructed for a charge of one drum (1,500 pounds) mixed acids and 210 pounds glycerol, it seems to meet the requirements of both practical and theoretical conditions. Of course, the size of the apparatus has to be such as not to allow any undue pressure to be exerted on the charge by confining the mixture and not so large as to allow a play of waste acid fumes to attack a large surface on the top portion of the apparatus.

Of late some so-called continuous apparatus have been proposed. I have never seen one in operation and cannot judge of their practicability. Knowing, however, how difficult it is to get the acid mixture uniform (on account of stratification of the acids), I doubt if they prove economical. If the jets of glycerol and acid mixture meet it is of the utmost importance that the latter should be of uniform composition and the difficulty of getting it so is within the experience of every manufacturer of nitroglycerol. If the acid is not continually stirred it will lack uniformity, and give a low yield, the temperature will fluctuate to a great extent and the danger of the manipulation will be greatly increased. Besides a small jet is easily stopped up and then in a few seconds the point of safety is overstepped.

#### SEPARATORS.

Formerly, when the cost of the nitroglycerol was of less importance; the nuisance of strongly acidulated water was not considered; and the yield was not all important; the charge was always drowned immediately after it was made. Now it is necessary to recover the "spent" acids, both for the reason of economy and so as to avoid the accumulation of acids, which otherwise would destroy whole tracts of land. On a small scale, when the apparatus only has to be used two or three times a day, it can also be used as a separator, but usually this is not the case, and such a number of separators has to be used as will permit the first one being emptied while the last one is being charged. For this reason the size of a separator ought to be such that it will hold exactly one charge of the converter.

The forms of separators have varied from that of a square box to that of a cylinder and a funnel. As they are generally made of heavy lead it is of advantage to present as few seams and corners as possible, and for this reason they should be made round so that only one seam is necessary. The funnel-shaped undoubtedly possesses several advantages, such as easy separation, but it takes too much space and must be made too deep to be convenient, if the nitroglycerol is to be skimmed off. An ordinary wooden tub, lined with heavy lead (ten pounds to the square foot), which at the bottom has an inclination of about six inches, or is drawn to a funnel-shape, answers the purpose very well.

The faucets of the separators, as well as of the apparatus, ought to be of earthenware, perfectly ground and well greased with vaseline, but the place to put them is hard to determine. The separation line of the nitroglycerol from the acids, varies considerably, partly on account of the difference in yield and partly because the amount of acid used frequently varies from three to four inches.

If the upper funnel be too high up it frequently happens that several inches of nitroglycerol remain and have to be dipped, and if it be too low the amount of acid drawn off would be a source of danger in the wash-house. If the charge is not too big the "dipping off" is accomplished in a short time and the constant stirring of the dipping pan (an enameled iron casserole) in the nitroglycerol helps the separation considerably. It is, however, necessary to have an experienced man in the separating room as the greatest loss is here, if the skinning is not conducted with the most scrupulous care. In most cases it is preferable to dip besides having faucets as every one of them, being brittle as they are, considerably increase the danger from breaking. The separation ought to be accomplished in an hour and a half. If it is not, the glycerol used has been inferior or the operation in the apparatus has been faulty. If the glycerol contains calcium or other alkaline salts and fatty acids there will be found a great number of worm-like particles floating up and down, mechanically carrying nitroglycerol to the acids and *vice versa*, and the charge had better be drowned. The last two inches in the separator should be drowned as it always contains enough acid to considerably raise the temperature of the first wash-water and here is where the funnel, the spout, or the inclined bottom is of advantage as it only allows a narrow separating belt. If the charge is run down in the separator at  $17^{\circ}$  to  $19^{\circ}$  C., it scarcely, if ever happens that the temperature rises again to any dangerous degree. It is indeed very rare that it happens that the temperature varies to a dangerous degree in the separators, but it is of the utmost importance to guard against such an occurrence and it ought to be made compulsory for the man in charge to note down the temperature registered at the thermometers in each separator every fifteen minutes, and any neglect

or omission in this respect should be followed by immediate dismissal, as it possibly endangers the life of every one connected with the manufacture.

Before the charge is allowed to leave the separator-house it should be immersed in, and for a few minutes stirred, with cold water, both for the reason of security and economy; of security, because the nitroglycerol mixed with even a small quantity of acid is liable to explode in the pipes in case a friction should take place, or some water be present to raise the temperature of the adherent acid and of economy, because the first wash-water will invariably carry along some nitroglycerol, which ought to go to the drowning tank where it will settle at the bottom of the tank.

#### WASH-HOUSE.

When it is considered how very important a thorough washing of the nitroglycerol is, what danger a poorly or insufficiently washed nitroglycerol is in the process of manufacture, and that it is an ever-increasing source of danger the longer it is stored, the question of a proper wash-house is one of great importance. As to the form of wash-tubs, the conical one is undoubtedly the best. This form admits the broadest possible surface of contact, it prevents any water coming with the nitroglycerol when it is drawn off, and affords a good opportunity for skimming or drawing off the wash-water. The size need not be larger than to easily accommodate one-half of the charge, because the man who washes has plenty of time to do this when the charges are settling. The wash-tubs as well as the faucets can be of wood (preferably cedar), which should be free from knot-holes, as so little acid comes along when a charge is well separated and has had a preliminary washing in the separator-house that it cannot attack the wood. When a charge is let down the water ought to be let down slowly and from a coil at the side of the wash-tub so as to give it an opportunity to bubble through the nitroglycerol.

If compressed air is to be had, that is, of course, the preferable stirrer, otherwise wooden stirrers can well be used. To prevent waste the wash-water, when drawn off, ought to be allowed to stand in a big tank as it always carries some nitroglycerol along, which will be deposited at the bottom of the tank and should be

taken out at least once a week. The amount of water to be used depends, of course, upon the size of the charge, but twice the volume of the nitroglycerol is certainly enough under all circumstances. If the charge has been well separated and a preliminary washing has been given it one washing will be enough. The last trace of acid should now be taken out. For this purpose a weak alkali solution is used. It is a convenient arrangement to have this solution in a tub set up somewhat higher than the wash-tub and let it run in by gravity, preferably through the coil which is used for the wash-water. If the water in this tub is kept at  $30^{\circ}$  to  $35^{\circ}$  C. and the water at this temperature is nearly saturated with sal-soda or if about five pounds of soda-ash are used to about fifty gallons of water the solution is of proper strength. Of this solution I have found that it takes about two pails to remove the last traces of acid in about 460 pounds of nitroglycerol. After the soda solution is drawn off the nitroglycerol should have one thorough washing with water and then it ought to be ready for use. To ascertain this, however, each and every charge should be tested. This of course can be done with any one of the ordinary indicators and the choice of one depends upon the intelligence and education of the man in charge of the washing. For any ordinary workman I would recommend the use of very carefully prepared litmus paper. This is more easily handled than most indicators and is quite sensitive. It must be kept in well-corked bottles and out of the acid fumes. The liquid indicators generally require more skill than the man in charge can be depended on to exercise. Two like strips of litmus paper should be used at one time, one dipped in a little distilled water (which the steam on hand always can furnish) and the other in the nitroglycerol and then be compared. When the wash-water tank is cleaned it will be found that a spongy, dark-gray substance has accumulated. This consists chiefly of salts from alkalies and fatty acids, and holds mechanically a good deal of nitroglycerol. To get this out a felt filter can be used, and by letting it stand long enough in this a good deal of nitroglycerol is obtained.

It is difficult to give a rule for the size of the drowning-tank. This depends upon the size of the converter and the charge used ;

the amount and composition of the acid mixture; the size of the separators and somewhat on the temperature of the water available. It must be large enough to allow one full charge to be drowned without the least danger. It would seem as if the larger the tank the greater the safety, but that is not so. If the tank is very big the very large amount of water it holds exerts a pressure, which is likely to spring either the bottom staves or the sides, or the faucets, and if this is done and the acidulated nitroglycerol comes in a crevice not reached by the water, it immediately attacks the wood, generating a heat which sets the nitroglycerol afire and the danger is considerable. It is hard to empty and clean a very large tank; such a tank will last a shorter time than a smaller one, and when it is to be replaced the cost is considerable and the time required, during which the manufacture must cease, is long. On the other hand, if the tank is too small, it is dangerous to drown a full charge; the water in the tank is always strongly acidulated from the last inches of the separators, which must be drowned and is consequently hard to dispose of and constant and tedious cleanings must be made. With these points in view it seems to me to be the best arrangement to have two medium-sized tanks for drowning-tubs connected in such a way that they are in constant communication but will allow each one to be disconnected from the other and connected with the apparatus, separators, and wash-house separately. The size of each one need then only be such that one alone will be enough for an emergency during the short time required to repair the other.

To ascertain the cost of the powder, to be able to check the carefulness of the men, and to rightly regulate the daily output it is of importance that the yield of nitroglycerol and the amount on hand can be easily ascertained at any time. I have found it convenient for this purpose to have the storage tank placed on a large platform scale, where it can be weighed at any time. It is weighed, the amount of nitroglycerol taken out since the last weighing is calculated from the formulas of the powder produced; the weight of tank and nitroglycerol at previous weighing deducted; and this amount divided by the number of charges run down; an average yield will thus be had. The storage tank



—to fit the platform scale—should be a square lead-lined box, and of such a size that it will hold enough nitroglycerol for the manufacture of high-grade dynamite even if three charges should be delayed in converter, separators, or wash-house.

I have found it most convenient to draw the nitroglycerol from the storage tank by means of a rubber hose long enough to reach the top of the tank when raised. If this hose be fastened by a clamp to the upper part of the tank it will not be necessary to have a faucet which must be turned every time a bucket is drawn and which is likely to give rise to considerable friction. By bending the hose sharply between both hands the nitroglycerol will be shut off until the end of the hose reaches the bucket, placed on a small platform scale some distance away, when it can be let down carefully in any desired stream simply by relieving the pressure. The mouth of the hose should, of course, be carefully wiped off before being put back into position.

The problem of conveying the nitroglycerol in the most careful manner from one house to another and from the storage-tank to the mixing-house is one that is astonishingly neglected in most powder works and yet it is one of the utmost importance. It is imperative that no communication by hose, pipes, or trays should exist between the buildings except during the time actually taken to run a charge from one to the other. In case of explosion or fire in one of the buildings the whole factory is doomed to destruction if connections exist between the buildings, but if the connections are cut off the plant can, without difficulty, be so constructed as to make one building independent of the other, as Professor Munroe's valuable experiments have clearly shown, that nitroglycerol is less liable to sympathetic explosion than was generally considered. The converter should be in direct communication with the drowing-tank, and not be allowed, as is so very frequently the case, to communicate with this by the way of the separating-house. This connection may be permanent as the danger of explosion in the drowing-tank is small, but for the sake of additional safety, may be broken near the apparatus. The connection between the apparatus and the separating-house may be made either of lead pipes or rubber hose, but in both cases it should be broken off at an equal distance

from both buildings, a space of at least twelve feet allowed between the ends of the pipes or hose, connection being made between the ends only when a charge is let down and disconnected as soon as the charge is down, and the upper end should terminate in a small lead-lined box to receive drippings. The same conditions should be observed between the separating-house and wash-house, and between the wash-house and storage-tank, and any failure to immediately disconnect the line after use should be severely reprimanded and repetition followed by dismissal. The connecting and disconnecting can be very easily accomplished by a piece of rubber hose and two short glass tubes.

To convey the nitroglycerol from the storage-tank to the mixing-houses pails are almost invariably used. These pails were formerly either of lead or of leather but indurated fiber buckets may be used, if precaution is taken to tare the buckets at least once a week since they are affected to a certain extent by the nitroglycerol.

It is necessary that the nitroglycerol plant with the storage-tank be kept at a considerable distance from the mixing or dynamite manufacturing plant and consequently these buckets have to be carried a long way. The rule not to have any connections between the houses is still more forcible when the connection between the storage-tank and the mixing-houses is considered; no pipe line between the plants should be admissible. In most cases the men have to carry these buckets by hand and a close supervision should be kept to ascertain that the men are careful in doing this, especially in slippery weather. Acting on the suggestion of Professor Munroe some three years ago Messrs. Roebbling & Sons built a trolley system to carry the nitroglycerol from the storage-tank to five different mixing-houses at the Forcite Powder Manufacturing Co.'s plant, in Hopatcong, N. J., and this plant worked perfectly satisfactory.

In the construction of a nitroglycerol plant it has always been maintained that it should be so located that the nitroglycerol may run down by gravitation from the converter to the storage tank. It is well and good if this can be done without inconvenience but it is in no way any absolute necessity, as it can easily

be arranged to press the nitroglycerol from one building to another with compressed air without any great cost and with perfect safety. The mixed acids should, if possible, be cooled off for some time in a place higher than the top of the converter, and if the time it takes to run a charge is allowed for in cooling the acids for the subsequent charge they will not need to be cooled off in the converter, which would otherwise delay the running, considerably. As the glycerol almost invariably has to be warmed before using to assure an even flow and as this operation can easily be done in the converter-house, it is necessary to afterwards press up the glycerol required to a receiver above the apparatus.

The safe distance between the buildings depends partly upon the nature of the ground, partly upon the amount kept in a building at one time, and partly upon the construction of the buildings themselves. The drowning-tank should be as near the converting-house and the separating-house as possible and so low as to assure the rapid discharge of a charge. If the ground is hard the shock of an explosion is more easily carried from one building to another than if it is soft or marshy and the buildings have then to be further apart. If the nature of the ground allows a natural protection of one house from another, or if artificial banks can be built between and at some distance from the houses the latter can, of course, be closer than when unprotected. The buildings ought to be constructed in the lightest possible manner so as to afford little resistance to an explosion, which would otherwise be too powerful. All the buildings must be ceiled and in every way so protected as to assure as even a temperature as possible, but the foundation, the framework, the roof, etc., can be of a very light material. In the separating-house, as well as in the wash-house it is to be recommended that the floor be lined with lead, as this materially assists in keeping the house scrupulously clean and prevents any adulterated nitroglycerol from creeping in between joints, a thing that must be carefully avoided.

To obtain a good yield of nitroglycerol, that is, to make power economically, the materials selected must be of the best quality or rather of the most suitable quality for the purpose.

To obtain and maintain this there is only one way open to the manufacture; *viz.*, to let a chemist of experience and standing draw up specifications for the acid mixture and the glycerol and to employ a chemist to see that the specifications are rigidly enforced. Some of the more prominent powder works in this country have now such specifications drawn and it would be of great benefit to the trade in general if they should be published so as to lay down a normal rule for the contractors. In this connection I wish to state that whenever it is practicable it is, without doubt, the most economical and best plan for dynamite works to make their own nitric acid. The iron drums, in which the acid mixture comes, are not affected by sulphuric acid but no one ever claimed that they are not affected by nitric acid, and it is hard to see why this should not be the case even when the nitric acid is mixed up with the sulphuric as it can hardly be claimed that the sulphuric acid is a preventive against such attack. It is so frequently lost sight of by manufacturers that the sulphuric and nitric acids are simply a mechanical mixture in which each one retains its peculiar chemical properties, and not a compound different from anything else. This mixture stratifies by standing, the nitric acid corrodes the drums, which are consequently weakened, and, worst of all, it may not be uniform in composition. The contractors frequently mix the acid in tanks in sufficient quantity to fill two or three car-loads. This mixture, which is drawn from the tanks to the drums, must, by necessity, be lacking in uniformity as the specific gravity of the sulphuric acid is so much higher than that of the nitric. It has come within my experience that when the supply of acid mixture was delivered at the beginning of the month instead of being distributed in weekly deliverances, the acid mixture in the drums which have been lying for four weeks has been very much inferior to that which was used in the beginning of the month and that consequently a bad yield resulted. If there were no other reason existing than that of getting a uniform mixture of acids it would be sufficient to advocate the erection of a nitric acid plant, but besides that it is decidedly more economical to have such a plant and it makes the manufacturer more independent both of contractors and of freight service.

To test the stratification of the acid mixture some glass jars four feet high and four inches in diameter were filled with an acid mixture of sixty-five per cent. sulphuric acid to thirty-five per cent. nitric acid and the mixture allowed to stand undisturbed for some time. In four days the color of the upper four to five inches had changed from a pale yellow to a brown color. After six days standing a sample taken six inches from the top had the composition of thirty-eight per cent. nitric acid and sixty-one per cent. sulphuric acid, and after twelve days an analysis gave thirty-nine per cent. nitric acid and 58.4 per cent. sulphuric acid. A sample taken at the bottom of a jar after six days standing gave sixty-eight per cent. of sulphuric acid and thirty-two per cent. of nitric acid, and after twelve days such a sample gave seventy per cent. of sulphuric acid and 29.3 per cent. of nitric acid. These figures represent the average of a number of analyses.

What is to be done with the spent acids and where to run the acidulated water from the drowning-tank and the wash-house are questions which well deserve attention. There exist at present three ways of using the "waste" acids each one of which has some merits. In Europe these acids are most frequently used for the manufacture of fertilizers. Where other fertilizing materials are scarce and insoluble phosphates are plentiful it is natural that the use of this acid for the conversion to soluble phosphate should flourish. The most usual way to utilize the "spent" acid in the United States has hitherto been to "regain" it. The ordinary way of doing this has been to pass the acid mixture through towers filled with coke or bricks where it is met by a jet of steam, which carries the nitric acid through the top of the tower and to receivers, leaving the sulphuric acid to run down to the bottom. The waste of this process is obvious. The sulphuric acid is diluted to such a degree as to make it almost valueless, and the nitric acid rarely acquires a strength of more than 32° to 44° B. The acids in the waste acid mixture has still considerable strength, and to dilute them in order to "regain" them is uneconomical. The third way is to use the mixture direct for the production of nitric acid. It contains nitric acid of the strongest kind, as all the water formed during the reaction has

been taken up by the sulphuric acid, and the sulphuric acid itself has not been diluted to such a degree that it is unsuited for nitric acid manufacture. If the mixed acids, therefore, be added to a charge of sodium nitrate and strong sulphuric acid, almost all of the nitric acid will be recovered. The objection always raised to this plan is that the mixture may contain some traces of nitroglycerol, which would endanger the process. In answer to this it can be said, first, that very little nitroglycerol need be present if the separation has been carefully conducted, and if the acid has been allowed to stand (preferably cooled) for some time before using; secondly, that the very small amount remaining can be exploded by detonating a strong cap in the vessel in which it is stored before using; and thirdly, that even if present in a considerable degree in the retort it would all be decomposed there by the sulphides formed, which are the best decomposers of nitroglycerol known. This way of utilizing the "waste" acid is one of the most economical that can be devised. Unfortunately, however, it only applies to factories having nitric acid works of their own. If the waste acid is kept in iron vessels with free access of air, the vessel will soon be attacked, but if the air is excluded it is not affected. I was brought to this conclusion by observing acid drums a few years ago and to ascertain how far this was true the following experiment was carried on: A small iron still, previously weighed and heated with an iron coil was filled to two-thirds with "waste" acids and connected with a vacuum pump. The acids were now boiled down to about one-half of the still by steam-heat in vacuo. The acid was tested and it was found that the sulphuric acid was of sufficient strength for immediate use and the nitric acid was as strong as before using, but about twenty-four per cent. of the original acid was gone. By adding strong nitric acid to this mixture in such amount as to re-establish the proportion between sulphuric and nitric acids the acid may be directly used again. The still had, after repeated use, lost almost nothing in weight, showing that it was not affected by the acids under this condition. Continued experiments in this direction may give a solution to the problem of how to economically use the waste acids in works which have no nitric acid plant. To pay freight for a strong

nitric acid, use part of it, dilute the rest, and pay another freight back to the factory from where it came, as is done where regaining works are used is certainly not economy.

The acidulated water from the drowning-tanks, wash-house, etc., is frequently a source of great annoyance to the nitroglycerol manufacturers. It cannot be let down into running water as it will soon pollute this; it cannot be run into the field as it will soon destroy all vegetation and cause complaint from all sources. If a deep ravine, separated by considerable earth banks from water supplies is to be found on the ground it may be run into that. The ravine, however, ought to be thoroughly cleaned from leaves, etc., and the bottom scraped so as to enable the soil to absorb the water quickly. If limestone of any kind is to be had on the grounds or near by it is certainly the best way to blast a big excavation, fill it with the limestone, and let the wash-water run into this. The limestone will purify the water from adherent nitric and sulphuric acids and affords a good drain for the water.

How far the risks of the dangerous manufacture of nitroglycerol can be minimized may be judged by the fact that since 1871 no accident of any kind, explosion, or fire has taken place at Winterwiken, Stockholm, Sweden. What is of the utmost importance is to have well-constructed plants, good supervision, and a good chemical knowledge.

COLUMBIAN UNIVERSITY,  
December, 1894.

## METHODS FOR THE EXAMINATION OF GLYCEROL FOR USE IN THE NITROGLYCEROL MANUFACTURE.<sup>1</sup>

BY G. E. BARTON.

Received January 2, 1895.

**T**HE most commonly accepted methods for the examination of glycerol are described by Allen in his *Commercial Organic Analysis*, Vol. II.

His requirements are very severe, in fact, too severe it seems to me in some respects. For example, he requires entire freedom from chlorides and iron. Most of the glycerol offered to the

<sup>1</sup> Read at the Boston Meeting, December 28, 1894.

nitroglycerol trade contains both these impurities and, in limited amounts, they are not harmful. He also requires only feeble reaction with basic lead acetate, yet distilled water gives a decided reaction with this reagent.

It is not possible, using the methods of examination Allengives, to accurately describe a glycerol suitable for the manufacture of nitroglycerol.

The different impurities that such glycerol is liable to contain are:

1. Inorganic bodies, other than sodium chloride, which are shown accurately enough for technical purposes by the ash determination.
2. Sodium chloride.
3. Carbohydrates, sometimes used as adulterants, which are shown by the carbonaceous residue.
4. Fatty acids, either free or combined, a measure for which is found in the total acid equivalent or saponification number.
5. Lighter bodies, mainly hydrocarbons, which influence the permanent specific gravity quantitatively.

The following methods of examination are the result of several years' experience in the examination of glycerol intended for use in the manufacture of nitroglycerol.

*Ash and Carbonaceous Residue.*—Weigh out between four and one-half and five and one-half grams of glycerol in a tared porcelain capsule and heat cautiously till it inflames. Remove the source of heat and allow it to burn away. Transfer the capsule to a desiccator and, when cold, weigh. This gives the weight of the carbonaceous residue.

The carbonaceous residue ignited gives the ash.

*Sodium Chloride.*—Take 100 cc. of glycerol, transfer to a porcelain casserole, rinse with distilled water, and add the rinsings to the contents of the casserole. Dilute to 300 cc., neutralize any free acid with sodium carbonate, add normal potassium chromate solution till the contents of the casserole have a decided yellow color, and titrate with tenth normal silver nitrate solution. After deducting two-tenths cc. required to give the coloration, the remainder is calculated to sodium chloride. The weight of glycerol taken is calculated from the number of cubic



centimeters, using the specific gravity at the temperature of the room.

*Total Acid Equivalent.*—One hundred cc. of glycerol are taken for the determination, transferred to a beaker, made up to about 300 cc., a few drops of a one per cent. solution of alcoholic phenolphthalein added, and then ten cc. of normal sodium hydroxide. Boil for a short time and then run in normal hydrochloric acid till the pink color is discharged. The result is expressed in grams of sodium hydroxide required by 100 cc. of glycerol.

*Higher Fatty Acids.*—Pass a stream of nitrogen tetroxide through a portion of the glycerol diluted with twice its volume of distilled water, then heat on a steam-bath for two hours. If there is no precipitate formed, either on diluting or later in the operation, the glycerol may be considered free from higher fatty acids. Glycerol intended for use in the manufacture of nitroglycerol should stand this test.

*Neutrality.*—A glycerol may be considered neutral if, when fifty cc. are diluted with 100 cc. of water and a few drops of an alcoholic solution of phenolphthalein added, not more than three-tenths cc. of normal hydrochloric acid or normal sodium hydroxide solution is required to produce the change in color.

*Specific Gravity.*—For the specific gravity determination, a Sartorius specific gravity balance is used, and the determination is made at the temperature of the room. The value found is reduced to the value at 15° C. by adding a product represented by  $(t-15) \cdot 0.00065$  and subtracting from this sum a number represented by  $0.0003 + (t-15) \cdot 0.000025 R$ , when  $t$  is the temperature at which the work is done, read from a thermometer in the glycerol, and  $R$  is the value read from the balance.

*Permanent Specific Gravity.*—Heat a sufficient portion of glycerol for a specific gravity determination in a 250 cc. flask for two hours, at a temperature between 225° and 230° C. At the end of this time allow the glycerol to come to the temperature of the room, keeping the flask corked with a stopper having a small opening for equalizing the pressure. The specific gravity is then determined as before described. The result is the permanent specific gravity at 15° C.

A good sample for nitroglycerol purposes tested as follows: ash, trace; carbonaceous residue, 0.012 per cent.; sodium chloride, 0.002 per cent.; total acid equivalent, 0.05347; permanent specific gravity, 1.2653; specific gravity, 1.2634; higher fatty acids, none; reaction, neutral.

I am indebted to Dr. Joseph Van Ruymbeke, the inventor of the Van Ruymbeke process of recovering glycerol from soap-lyes, for the first idea of the total acid equivalent and permanent specific gravity determinations.

THE COLUMBIAN UNIVERSITY,  
December 17, 1894.

### ESTIMATION OF TELLURIUM IN COPPER BULLION.<sup>1</sup>

BY CABELL WHITEHEAD.

Received January 2, 1895.

**D**ISSOLVE from twenty-five to fifty grams of the bullion in nitric acid 32° B. and boil off the excess of acid. Add to this solution an amount of a ferric nitrate solution equivalent to 250 mgms. of metallic iron. Precipitate, while hot, with an excess of ammonia, filter, and wash with dilute ammonia until the copper salts are entirely removed, redissolving and reprecipitating if necessary. The residue on the filter contains the tellurium and selenium present in the bullion as ferric tellurites and selenites. This is dissolved in hydrochloric acid, and excess of tartaric acid added, the solution made alkaline with potassium hydroxide, and hydrogen sulphide passed through it, when the tellurium and selenium pass into solution as soluble sulphides. Filter; decompose the alkaline sulphides in the filtrate with dilute hydrochloric acid; allow the liquid to stand in a warm place until the hydrogen sulphide has been removed. Filter again; dissolve the tellurium and selenium sulphides in aqua regia; evaporate the solution to dryness, take up with hydrochloric acid and precipitate the tellurium and selenium from the solution by passing sulphur dioxide through to saturation. Cover the beaker and allow the solution to stand for twelve hours in a warm place, when the precipitate, which consists of tellurium and selenium, is filtered on a tared filter, dried at 100°, and weighed together.

<sup>1</sup> Read at the Boston Meeting, December 27, 1894.

The selenium is separated from the tellurium by boiling the precipitate in concentrated potassium cyanide solution, filtering, and adding hydrochloric acid, when the selenium comes down as a brick-red precipitate, which is weighed as before, after drying at  $100^{\circ}$ .

The tellurium is determined by difference or the small amount dissolved by the cyanide solution may be precipitated, after removal of selenium, by saturating with sulphur dioxide, collecting the precipitate with the original residue, and weighing after drying at  $100^{\circ}$ .

THE COLUMBIAN UNIVERSITY,  
WASHINGTON, D. C.

---

## THE USE OF SULPHUROUS ACID ( $\text{HNaSO}_3$ ) IN MANUFACTURE OF GLUCOSE SYRUP AND GRAPE-SUGAR.

BY HORACE E. HORTON.

Received January 16, 1895.

UP to the year 1893 a large quantity of the glucose syrup and grape-sugar offered in home markets was manufactured by a carefully worked-out process, in which sulphurous acid had but little if any place.

While a fine grade of glucose can be manufactured without the use of sulphurous acid, its irrational use has taken full possession of some manufacturers.

That sulphurous acid has a legitimate place in a rational process of manufacture few who have studied the subject will deny, but a great deal of careful work is yet necessary to define the use of this reagent.

I have studied the action of sodium bisulphite on glucose syrup and grape-sugar in several directions, and with interesting results. The bisulphite used was manufactured by Gelian and Co., of New York, who have an excellent article of  $38^{\circ}$ - $40^{\circ}$  Bé. density.

*Preserving Color of Glucose Syrups.*—Numerous experiments have convinced me that sulphurous acid is of great value in preserving the color of glucose syrups. I will present here one

experiment, from the many made, to demonstrate this action of the acid.

On June 21st, fifteen batches (ca. fifty barrels each) glucose syrup were manufactured. Batches 2-9 received one gallon 38° Bé. sodium bisulphite and eight fluidounces of muriatic acid; batches 10-15 received two gallons bisulphite and sixteen fluidounces of muriatic acid.

On July 7th, batches 2-9 had lost color and brilliancy. Batches 10-15 of good color and brilliant.

In September batches 2-9 had a *decided* brown color and had lost brilliancy through separation of gypsum (?). Batches 10-15 good color but not brilliant.

In January, batches 2-9 had a *dirty brown* color. Batches 10-15 a *light* straw coloration.

The bisulphite may be added all to the finished product in the cooler, or a part to the liquor in the 39° Bé. vacuum pan, and the remainder to the finished product in the cooler.

The effect of its addition to the 39° Bé. liquor is immediately perceptible in the bleaching of the light straw-colored liquor.

*Giving Brilliancy to Candy.*—The candy test is for brilliancy and color, and while in some hands gives meaningless results, in skilled hands is a valuable criterion.

This test is carried out as follows: The glucose is weighed into a shallow copper dish along with cane-sugar ("Havemeyer and Elder S. R. Co. 'A' Sugar"), and 150 cc. water added. The proportions of glucose and cane-sugar are the following: For

42°	Bé. syrup,	8 oz.	glucose and	1 lb. 9 oz.	cane-sugar;
43°	"	"	8 "	"	" 1 " 10 "
44°	"	"	8 "	"	" 1 " 11 "
45°	"	"	8 "	"	" 1 " 12 "

The dish is placed over the direct flame of an eight-inch Fletcher burner and when the mixture begins to boil, five drops of olive-oil are added to prevent trouble from bubbles. Continue boiling for six minutes, watching carefully the rise of temperature with an accurate thermometer, and when 308° F. is reached, which usually requires nine minutes, pour the hot mass on an

oiled marble slab, when it spreads over the surface, making an irregular circular mass of about fourteen inches diameter.

When the mass has cooled sufficiently *to cut*, divide into halves. Mold one-half into a slab one inch thick, five to six inches long, three inches wide, and wrap in an oiled paper.

The other half is to be cut into strips one to one and a half inches wide, and *without any manipulating*, folded over four times, forming a coil.

From the slab and coil the brilliancy and color are judged. Using a confectioner's glucose made by oxalic acid and run over a dull specially prepared bone-black, a standard candy was prepared having the necessary brilliancy and color.

A large number of glucose samples from sharp bone-black, dull bone-black, specially prepared phosphate bone-black with bisulphite and without bisulphite were made into candy, and in every instance the addition of bisulphite added brilliancy and color.

In connection with candy I must speak of the bugbear sticky candy; there is a great hue and cry attributing sticky candy to the use of bisulphite. I am unable to trace the origin of this assertion to any person, but all are confident of its truth. It may have originated in the practice of preparing syrup for gum-drop manufacturers by adding two and a half buckets of bisulphite and one and a half quarts of muriatic acid to a batch of forty-four barrels 42° Bé. glucose, thus producing an acidity of 0.05–0.055 gram hydrochloric acid in 100 grams syrup. The reasoning may be. If sticky, moist gum-drops are produced by syrup receiving a large quantity of bisulphite, then stickiness and moistness in *all* candy must be due to the use of bisulphite!

I have studied this subject carefully and have been unable to trace sticky candy to the use of bisulphite.

Six samples of candy were boiled using 43° Bé., confectioners' glucose containing two gallons of bisulphite to fifty barrels; six samples of candy using glucose containing eight gallons of bisulphite to fifty barrels.

Three of the candies made from glucose containing two gallons, and three from that containing eight gallons, were exposed

on the laboratory table. Six samples were placed in a closely covered desiccator over sulphuric acid.

It was observed that the samples exposed on the laboratory table grew equally sticky; the samples in desiccator showed no sign of stickiness. This pointed to a certain degree of humidity of the air influencing the stickiness of candy. With this in mind a long series of careful observations were made with reference to the relative humidity of the air, and with the result that stickiness cannot be attributed to the use of bisulphite.

It is interesting to note here, that one candy manufacturer will complain of glucose giving sticky candy, while another manufacturer using glucose from the same batch makes no complaint.

Again, for some unknown reason, it is supposed that glucose receiving over three gallons of bisulphite per batch cannot be used by candy manufacturers for sundry *unknown reasons*! To obtain data bearing on this, batches of glucose were prepared containing five, six, seven, and eight gallons of bisulphite and placed in the hands of a skilled candy manufacturer who knew nothing of the content of bisulphite. In every instance, glucose containing eight gallons of bisulphite gave the best results!

*Influence of Bisulphite on Boiling-Point of Candy.*—The use of a large quantity of bisulphite makes it possible to boil candy to a higher temperature than when no bisulphite or a small quantity is used.

Batches of confectioners' glucose, 43° Bé. density, were prepared from a sharp bone-black and received varying quantities of bisulphite. Candies were boiled and with the following results:

Batch receiving 2 gals. $\text{HNaSO}_3$	boiled to 308° F.	Candy good color.
" " 2 "	" " " 330° "	" " very bad color.
" " 6 "	" " " 308° "	" " very good color.
" " 6 "	" " " 330° "	Color better, but bad.
" " 8 "	" " " 308° "	Very good color.
" " 8 "	" " " 330° "	Color improv'g but bad.
" " 10 "	" " " 308° "	Very good color.
" " 10 "	" " " 330° "	Color still better.
" " 12 "	" " " 308° "	Very good color.
" " 12 "	" " " 330° "	Good color.

In the manufacture of hydrated grape-sugar having the average composition,

Red substance .....	70.00	per cent.
Water.....	20.00	"
Ash.....	0.52	"
Rest of dextrine.....	....	"
Nitrogenous bodies, etc.	9.48	"

---

100.00

---

it will be found that liquor from the second filtration can be treated with sulphurous acid to good advantage; and this accomplished by burning sulphur in a small iron furnace and pumping the fumes into the liquor.

Working with an amount of liquor representing 24,000 pounds finished product, the acidity when

1	lbs. sulphur is burned, is 0.016 gram HCl in 100 grams.
1 1/2	" " " " " 0.027 " " " " "
2	" " " " " 0.034 " " " " "

The use of bisulphite with glucose syrup made it easy to ask the question, What effect will bisulphite have on grape-sugar solutions? Tradition has it that an acidity of over 0.034 gram hydrochloric acid is not allowable; why, no one knows. Some claim that an acidity over this point interferes with the action of the yeast in brewing.

I have experimented in this direction and with the following result:

To batches of grape-sugar sulphured by burning one and a half to two pounds of sulphur and two gallons of bisulphite were added. Laboratory experiments failed to show a diminished activity of the yeast; and more convincing, the brewers using the sugar made no complaint.

It is reasonable to suppose that the slight acidity of 0.034-0.045 gram hydrochloric acid will be taken care of by the calcium carbonate present in water used for brewing.

The addition of bisulphite to grape-sugar solutions led to the interesting observation that crystallization is thereby accelerated. I have made long series of observations and the records clearly show this fact.

I will present a few observations on the subject :

No. of experiment.	Date of manufacture.	Date of observation.	Condition of sample with $\text{HNaSO}_3$ .	Condition of sample without $\text{HNaSO}_3$ .
1.	9.12	9.20	Hardened	Liquor on top
2.	9.11	9.20	"	"
3.	9.19	9.20	Heavy cloud of crystals	No cloud
		9.23	Solid	"
4.	9.23	10.4	"	Little syrup
5.	9.23	10.4	"	Considerable syrup
6.	9.23	10.4	"	Little syrup
7.	9.22	10.4	Little syrup	Great deal of syrup
8.	9.22	10.4	Solid	Little syrup
9.	9.22	10.4	"	Moist
10.	9.22	10.4	"	Very little syrup
11.	9.22	10.4	Plenty syrup	$\frac{1}{2}$ syrup
12.	9.21	10.4	Solid	$\frac{1}{2}$ "
13.	9.21	10.4	"	Mushy
14.	9.21	10.4	"	Little syrup
15.	9.21	10.4	"	$\frac{1}{2}$ syrup
16.	6.21	10.4	$\frac{1}{2}$ syrup	$\frac{1}{2}$ "
17.	9.20	10.4	Very little syrup	$\frac{1}{2}$ "
18.	9.20	10.4	$\frac{1}{2}$ syrup	$\frac{1}{2}$ "
19.	9.20	10.4	Solid	$\frac{1}{2}$ "
20.	9.20	10.4	$\frac{1}{2}$ syrup	$\frac{1}{2}$ "
21.	9.20	10.4	Little syrup	$\frac{1}{2}$ "
22.	9.19	10.4	$\frac{1}{2}$ syrup	$\frac{1}{2}$ "
23.	9.19	10.4	Solid	$\frac{1}{2}$ "
24.	9.19	10.4	Solid and dry	$\frac{1}{2}$ "
25.	9.19	10.4	$\frac{1}{2}$ solid	$\frac{1}{2}$ "
26.	9.19	10.4	$\frac{1}{2}$ solid	$\frac{1}{2}$ "

The bisulphite bleaches grape-sugar solutions readily, and its effect on the sugar at the end of fourteen days and after six months is very marked.

Added to the "washer batch" (the batch first dropped from vacuum pan after boiling out with muriatic acid) the effect is pronounced.

TOPEKA, KAN., January 8, 1895.

## THE FURFUROL-YIELDING CONSTITUENTS OF PLANTS.

By C. F. CROSS, E. J. BEVAN, AND C. BEADLE.

Received February 13, 1894.

THE chemistry of the formation of the permanent tissue of plants may be approached from various points of view. From the incidents of our working connection with the subject



of cellulose we have, from time to time, dealt with the anterior problem of its elaboration from the point of view of the hexosan complexes which are grouped under this term. De Chalmot, Stone, and others who have followed the pioneering work of Tollens, have been more especially confronted with the relation of the pentoses to plant structure and their life history, and have contributed a very valuable series of investigations now resulting in convincing proofs of important points hitherto of doubtful interpretation.

In the convergence of these two lines of investigation an issue has arisen, and a fundamental problem has become a subject of controversy chiefly between de Chalmot and ourselves.

We have maintained the position:

(1) That the furfural-yielding constituents of plant tissues are not to be regarded as necessarily and exclusively pentoses or pentosans, since there are oxyderivatives of the hexoses, themselves also C<sub>5</sub> compounds, characterized by the same reactions.

(2) That having regard to the chemistry and physiology of assimilation and cell-respiration in plants, it was probable that the celluloses common with other hexosans would be modified by oxidations of various kinds, these oxidations being probably attended by further combination of the products of oxidation with the parent complex, *i. e.*, with the unchanged residues of the complex.

(3) That, therefore, we may expect to find in the celluloses, furfural-yielding groups, *not* pentoses.

Upon the subsidiary question as to whether the actual formation of furfural is not always preceded by a change to a pentose configuration with elimination of the fully oxidized C. position, we expressed no opinion. It is, in fact, altogether irrelevant to the point at issue, which is simply that of the molecules as occurring in the plant tissue.

The controversy has proceeded by stages in the following publications, which we cite in order of time.<sup>1</sup>

The purpose of this communication is to point out, as briefly

<sup>1</sup> Cross, Bevan, and Beadle, *Ber d. chem. Ges.*, 26, 3520; 27, 1061; De Chalmot, 27, 1489, 2722.

as possible, that de Chalmot, in his latest communication,<sup>1</sup> closes the controversy in a manner satisfactory to ourselves, although appearing still to join issue with us. It is very necessary to quote two paragraphs from the paper:

(1) p. 589. "*Are there pentosans in plants which are formed from seeds which germinate in darkness?* It has become necessary to answer this question since Cross, Bevan, and Beadle, in a recent article, assert that the furfural-yielding compounds in the sprouts, which are developed from barley in darkness, are so-called oxycelluloses and are not pentosans."

(2) p. 610. "I wish now to put forward the following hypothesis: Pentose molecules are formed in complex molecules of hexosans (celluloses and hemi-celluloses), in which a part or all of the aldehyde groups have been bound by condensation and are thereby preserved from further oxidation."

This is precisely all that we have contended for. The second paragraph is the answer, from our point of view, to the question contained in the first.

We are dealing, in fact, with an oxycellulose series and the only remaining point at issue between us is this: We are of the opinion that the series is represented in the living tissues. De Chalmot holds that the pentoses are, as it were, explosively formed; the fully oxidized C. group preferring rather a summary exit than the alternative of combining with the basic or alcoholic groups of unaltered hexose or hexosan molecules. This view is, we think, at variance with the perspective of metabolism generally, and certainly contrary to what we know of the chemistry of the oxycelluloses, their very gradual formation under oxidizing treatment, and the intimate union contracted between the oxidized groups and unaltered molecules of the parent cellulose.

Since the final solution of the problem of the constitution of these "natural oxycelluloses" must take the form of quantitative resolution into molecules of simpler, if not the simplest form, it need not be further discussed *a priori*.

We are engaged in a study of their systematic dissection and the results will be communicated in due course.

<sup>1</sup> Am. Chem. J., 16, 589-611.

Of course, it will be understood that these criticisms in no sense lessen the value of the contributions of de Chalmot, and his fellow specialists in the subject of the pentosans, to the general problems of assimilation and metabolism. Any error which may have been made is one only of interpretation. The too free use of "pentose" and "pentosan" as the equivalent of "furfural-yielding constituents" will prove, we think, to have temporarily obscured some important points in the physiology of the elaboration of plant tissues, but there being now a substantial agreement in the main issue it may well be left to time and experimental investigations to "materialize" this further chapter in the life of the plant cell.

4 NEW COURT, LONDON, W. C.,  
January 30, 1895.

## THE SEPARATION OF SOLID AND LIQUID FATTY ACIDS.

BY E. TWITCHELL.

Received January 25, 1895.

THE fatty acids insoluble in water, which constitute the greater part of most natural fats, are probably always found as a mixture of two groups, one composed of saturated, the other of unsaturated compounds, the former belonging to the acetic series and the latter to the acrylic and other series containing still less hydrogen. In most fats of commercial importance, such as tallow, lard, cottonseed-oil, and some other vegetable oils, the first named group is represented by only two members, stearic and palmitic acids, which are solid at ordinary temperatures, while the last contains the liquid oleic and linolic acids.

An accurate separation of these groups ought to be the first step in the analysis of any fat, as without it other quantitative reactions, such as the amount of iodine absorbed or alkali combined by the fatty acids, would lead to no very definite conclusions regarding the actual composition of the mixture.

Although a number of analytical methods have been proposed to obtain this separation, their accuracy has not been without question, while in my work I have, at different times, attempted to separate solid from liquid fatty acids and entirely failed to obtain satisfactory results. It therefore seemed to me very

desirable to make a study of some of the methods which have been published, together with any modifications which might suggest themselves in the course of the work. In the following experiments it was attempted not only to compare the different methods, but to determine, if possible, by some direct test, the degree of accuracy of each.

Varrentrapp observed that the lead soap of the solid and liquid fatty acids show great difference in respect to their solubility in ether, soaps of the liquid acids being readily soluble, while those of the solid acids are almost, if not quite, insoluble. On this property of lead soaps have been based the methods which seem to promise the best results, though other solvents than ether have been recommended.

1. Perhaps the most carefully worked-out process is that of Muter, described in the *Analyst* of April, 1889, which has been employed in examining lard chiefly for the purpose of detecting an adulteration of cottonseed-oil or stearine. This method has been examined and slightly modified by Nathaniel J. Lane, who has published his results in this JOURNAL, February, 1893. According to this process, the neutral potassium soaps of the fatty acids in boiling water are precipitated by lead acetate. The lead soaps which adhere to the sides of the vessel are washed several times with boiling water, dried as quickly as possible, and then boiled with redistilled ether and allowed to cool thoroughly, filtered, washed, and the filtrate, containing the lead soaps of liquid acids, decomposed with hydrochloric acid and water. The ethereal solution of fatty acids floats on the acid liquid. An aliquot part of this solution is titrated with standard sodium hydroxide to determine the percentage of liquid acids, and another part is evaporated and dried in a current of carbon dioxide and treated with Hübl's solution. Muter finds about ninety-four per cent. as the amount of iodine absorbed by the liquid acids of lard.

Having carefully prepared the insoluble fatty acids of lard rendered in my laboratory (saponifying in the usual manner and decomposing with hydrochloric acid while avoiding exposure to air as much as possible), I carried out the process of Muter, following carefully all important details. A part of the ethereal

solution of liquid fatty acids obtained was put into a weighed Erlenmeyer flask provided with a ground-glass stopper; then dried on the water-bath in a strong stream of carbon dioxide, which had been washed by passing through sodium bicarbonate solution and dried over calcium chloride. After thoroughly cooling the flask, dry air was drawn through for a few minutes to remove carbon dioxide, and the flask weighed. The percentage of iodine absorbed by these fatty acids was then determined in the usual manner, the operation being conducted in the same flask. The object in finding the iodine absorption was to determine, at least comparatively, the purity of the liquid fatty acids, *i. e.*, their freedom from saturated compounds. The following iodine numbers were found:

	Iodine absorbed. Per cent.
Lard . . . . .	56.27
Fatty acids of lard . . . . .	{ 58.49 59.26
Liquid acid by above process . . . . .	94.06

In order to test the solubility of lead stearate and palmitate in ether, a mixture of stearic and palmitic acids, such as is found in commercial stearic acid, was purified by crystallization from alcohol till it gave an iodine number equal to zero. The lead soap was then prepared by the above-described method and a small quantity boiled twice with alcohol to remove free fatty acids and then treated with boiling ether and allowed to cool. At 25° C. 100 cc. of ether dissolve 0.015 gram of the lead soap, and this does not crystallize out at 0° C. This would cause an error of about one per cent. in the above process, while it is possible that, in the presence of lead oleate the solubility of the stearate and palmitate might be much greater.

Another and more serious objection to Muter's method consists in the unavoidable exposure of the lead soaps to the air. All my results seem to show that the lead soaps of the unsaturated fatty acids oxidize even more readily than the free acids. So that, though great care is taken to remove the liquid acids from the air, it does not seem possible to treat lead soaps in this way without a good deal of oxidation, especially during the tedious filtration. Fahrion has noticed this remarkably rapid

oxidation in the case of calcium soaps (*Chem. Ztg.*, 1893, 17).

2. In his book, *Chimie Analytique des Matières Grasses*, Jean describes a method of examining lard. This method—modified in the manner of treating the liquid acids—was next employed. Four grams of the same lard fatty acids were dissolved in fifty cc. of ninety-five per cent. alcohol; and to this was added two and a half grams of lead acetate dissolved in twenty cc. of the same alcohol, both solutions being hot. There was an immediate precipitate, and the mixture was allowed to stand one hour at the temperature of the laboratory, and then cooled to 15° C. and kept at this temperature one hour longer. A part was then filtered into a separatory-funnel, treated with ether and dilute hydrochloric acid, washed, and dried in carbon dioxide. The iodine number of these liquid fatty acids was found as in the previous experiment, and their percentage in the original solution calculated. The precipitate was washed thoroughly with ninety-five per cent. alcohol, decomposed with hydrochloric acid, and the solid fatty acids separated and weighed. Their iodine number was also obtained. The following were the results:

	Per cent. obtained.	Iodine absorbed. Per cent.
Solid fatty acids .....	46.24	4.90
Liquid fatty acids.....	51.82	103.37

These figures indicate a fractional precipitation in which all the solid and a part of the liquid acids are precipitated. The iodine number of the solid acids and the low yield of liquid acids both point to this. That part of the liquid acids in the solution is probably held there by the acetic acid liberated. This must be the case as lead oleate is only slightly soluble even in absolute alcohol.

If the liquid acids, precipitated along with the solid, consisted entirely of oleic acid as was probable, the iodine number of the liquid part of the fatty acids would be somewhat lower than 103.37 per cent. Yet the amount of liquid acids precipitated being in this case quite small, could only reduce the result by two per cent. at the most. The great difference between this iodine number and that of the liquid acids obtained by Muter's method show that the latter must have contained a considerable amount either of saturated or of oxidized fatty acids.

Jean gives the iodine number of the liquid acids of lard as 92.71. This low figure may be accounted for by the fact that he does not take the precaution to dry the fatty acids in a current of carbon dioxide.

3. It appeared desirable to determine first, whether the liquid acids obtained by the last process were entirely free from solid acids, and second, whether the precipitation was actually a fractional one, more or less of the liquid acids precipitating according to circumstances of temperature, concentration, etc. In order to decide these questions, four grams of lard fatty acids (prepared at another time and from another sample of lard) were dissolved in ninety-five per cent. alcohol and precipitated with lead acetate, cooled for one hour to 15° C., and filtered. Ten cc. of the filtrate were drawn off, decomposed with hydrochloric acid, the fatty acids dried in carbon dioxide, and treated with Hübl's solution as before, while the remainder of the filtrate was cooled for one hour to 0° C. At this temperature there was an additional precipitate. This precipitate was filtered off and washed with ninety-five per cent. alcohol, the washings being thrown away. The fatty acids obtained from the filtrate were also treated with Hübl's solution. The iodine absorbed by the fatty acids of these fractions was as follows:

	Amount obtained.	Iodine number.
Lard fatty acids		62.57
Fatty acids from filtrate at 15°	0.2675 gram (46.81 %)	109.35 per cent.
" " " precipitate at 0°	0.1020 "	
" " " filtrate at 0°	0.1915 "	118.02 per cent.

The fatty acids obtained from the precipitate at 0° chilled at 0° C. and melted at 7° C. It could therefore contain little or no solid acid, and was probably pure oleic acid. Its iodine number was not determined, but calculating from the iodine number of the filtrate at 0°, it must be very nearly 90—that of oleic acid—to make the iodine number of the mixture 109.35.

It is plain from the above results that the precipitation of fatty acids by lead acetate in alcohol is not a quantitative separation but a fractional precipitation, in which the solid acids are precipitated first, then oleic acid, and finally linolic acid.

Though no quantitative separation of the liquid acids has been

made, their percentage can be calculated as follows: The percentage of liquid acids in the alcoholic filtrate is calculated from the fraction drawn off. This is multiplied by the iodine number of these fatty acids. The result is deducted from the iodine number of the original fatty acids. The difference represents oleic acid. Dividing this by 0.9 gives the percentage of oleic acid precipitated with the solid acids. Adding this to the liquid acid in the filtrate gives the total liquid acid. In the case of the last sample the calculation is: 46.81 per cent.  $\times$  109.35 per cent. = 51.19. Deducting from 62.57 gives 11.38. Divide by 0.9 = 12.64, oleic acid in precipitate; add to 46.81 gives 59.45, total liquid acids; whose iodine number is  $\frac{62.57}{59.45} = 105.2$ .

The linolic acid is easily calculated from the iodine absorption of the liquid acids—109.35 represents 78.5 per cent. oleic acid, 21.5 linolic acid.  $21.5 \times 46.81 = 10.06$  per cent. linolic acid in the original fatty acids.

4. A process described by Röse (*Repert. f. analyt. Chem.*, 1886) consists in shaking the ethereal solution of fatty acids with finely powdered litharge, when the lead soaps are formed and those of the liquid acids remain in solution. This method was next employed, using not ether, however, but petroleum ether, completely volatile at 80° C., in which I had found lead stearate and palmitate to be much less soluble than in ether. 100 cc. of petroleum ether at 30° C. was found to dissolve 0.0034 gram of the mixed soaps while at 5° only 0.0018 gram were dissolved. Two and a half grams of the lard fatty acids used in the last experiment were dissolved in fifty cc. of petroleum ether, two and a half grams of lead monoxide added, and allowed to stand two hours in a warm place with frequent agitation. A fifty cc. flask was used having a graduated neck. It was filled almost to the stopper in order to avoid the oxidizing effect of the enclosed air. After two hours time the yellow lead monoxide had become white in appearance, due to the formation of lead stearate and palmitate, and the precipitation was judged to be complete. It is clearly not necessary to combine the lead with all the fatty acid. If a part of the liquid acids are in the form of lead soaps this will be a guarantee that all the solid acids have combined. The presence of lead in the filtrate will show



whether the agitation has been continued long enough. Before filtering, the flask was placed in ice-water for half an hour in order to insure as complete a precipitation as possible. Then it was filtered, a definite part of the original volume pipetted off, decomposed with hydrochloric acid in a separatory-funnel, and evaporated and dried in a current of carbon dioxide as before. The liquid acids calculated to the whole solution yielded 55.10 per cent. having an iodine number of 108.66. The precipitate on washing then decomposing with hydrochloric acid gave 44.70 per cent. solid acids having an iodine number of 3.02 per cent. This impurity was probably caused by an oxidation of the liquid acids to compounds whose lead soaps were insoluble in petroleum ether.

The results obtained here are not far from those calculated by the alcohol method. The petroleum ether method would have the advantage over the other in that the iodine number would be that of the liquid acids and not only of a fraction from which part of the oleic acid has been precipitated. On the other hand a quantitative result by the petroleum ether method could only be arrived at where the fat is perfectly fresh and the greatest precautions have been taken to avoid oxidation during the whole manipulation. The same sample of lard fatty acids, after standing seven days in a closed jar, gave the following results :

	Iodine number.
Solid acids.....	10.1 per cent.
Liquid " .....	101.7 "

The oxidation had given products both soluble and insoluble in petroleum ether ; and in this case the percentage of liquid acids cannot be inferred from the analysis.

A precipitation of all the solid and part of the liquid acids by lead acetate in alcohol, by the method described by Jean, with the addition I have proposed of finding the iodine number of both the original fatty acids and those in the solution, and calculating therefrom, would give accurately the percentage of solid and liquid acids in a fat. Such a method would perhaps be too cumbersome for general commercial work. Still I believe it is at present the only positive solution of the problem.

## IMPROVED METHODS OF WATER ANALYSIS.

BY IRVING A. BACHMAN.

Received January 2, 1895.

WE have in the South Atlantic States incontestable evidence that the true source of malarial disturbance is to be found in the water, and not in the air, as was formerly supposed. The introduction of deep-seated artesian wells has very materially decreased this trouble, and has rendered localities that were notoriously unhealthy, perfectly healthy.

The examination into the exact difference between the malaria-producing waters and those proof against it, has had the writer's attention for over two years, and the work herein detailed is a portion of the preliminary work looking into the best methods of analysis.

My experience with the Wanklyn process as ordinarily carried out with the usual apparatus, so impressed me with its crudeness, that for a long time I have had little confidence in the results I obtained. The loss by imperfect condensation, the crude way of adding the permanganate solutions, and the open-air contamination of the distillate are by no means in keeping with accurate work. The loss by imperfect condensation is very much greater than we permit ourselves to believe, and with the original Wanklyn process<sup>1</sup> is a very difficult matter to control; the loss is variable, and is dependent upon the rate of distillation and the efficiency of the cooling apparatus. After making a long series of experiments upon every character of material liable to be found in water, I am satisfied that a rate exceeding fifty cc. in fifteen minutes is accompanied by loss. As a modification of the Wanklyn process, Mallet<sup>2</sup> proposes to keep the original volume of liquid in the retort constant by the systematic addition of ammonia-free, distilled water, in order to prolong the action of the permanganate; this is objectionable, inasmuch as the operation is endangered by a constant source of error in the addition of ammonia-free water, which is difficult to obtain in so large a quantity.

<sup>1</sup> Wanklyn and Chapman Water Analysis, (6th ed.), 1884, pp. 38-40.

<sup>2</sup> Report National Board of Health, 1882, p. 210.

In my own work I had frequently noticed that the evolution of ammonia very often increased as the liquid in the retort became more concentrated.

Acting on this observation it occurred to me that by the action on a smaller and limited quantity of water by the full strength of the permanganate solution and supplying the water under examination at about the rate of distillation, very much better results could be obtained ; this I have now confirmed by a great many comparative analyses.

The apparatus used is shown in Fig. 1, and consists of distillation flask A, of one liter capacity, into which is fitted by a ground joint the remainder of the apparatus (this is the only

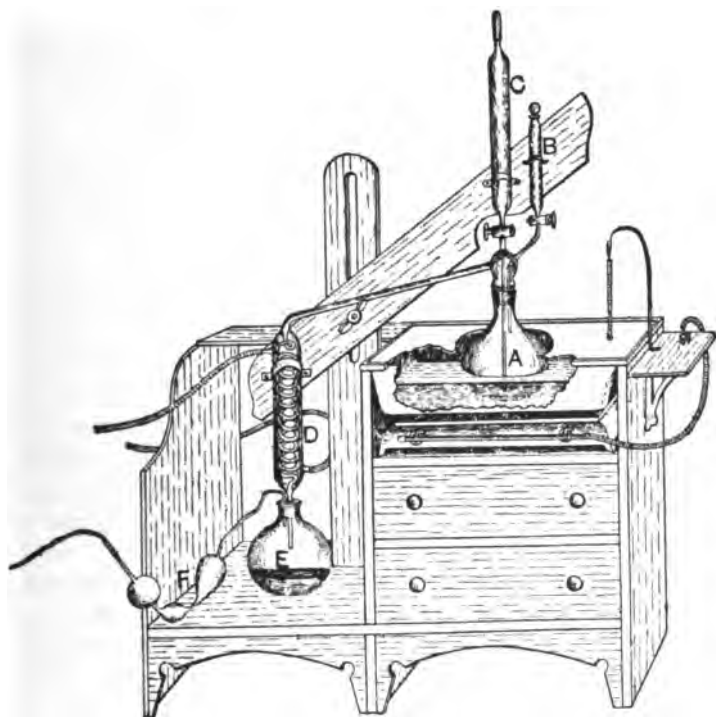


FIG. 1.

connection the apparatus has) ; through the bulb of the neck we have two burettes with stop-cocks, the smaller, B, with a capacity of fifty cc., with its tube projecting within three inches

of the bottom of the distillation flask; the larger burette C, has a capacity of 250 cc. and its tube projects to within one-half inch of the bottom. The cooling apparatus D, is a closely coiled glass worm, with a long projection at the lower extremity, to which is attached the distillate vessel E, by a soft rubber stopper, which also has tube for connection with the Will and Varrentrapp absorption bulb.

The apparatus is constructed to work under greatly reduced pressure, and the connection with distillation flask, as well as the stop-cocks, are accurately ground to remain tight without a lubricant.

The apparatus is mounted as shown, raised and lowered into the bath by means of a thumb-screw, as indicated. The whole is very easily managed, and is very serviceable. I have made over a thousand determinations with mine, and there is no reason why it will not continue to do good service for a very long time to come.

The heating of the apparatus is effected by setting the flask into a fixed saline-bath, with a covered top as shown, and heated from below by a two-pipe gas-burner.

*Mode of Procedure.*—After thoroughly rinsing the apparatus with ammonia-free distilled water, 500 cc. of the water under examination are put into the flask and the apparatus connected and lowered into the bath, the distillate flask with Will and Varrentrapp bulb, the latter previously charged with Nessler solution, are now attached and connected with the pump.<sup>1</sup> The partial vacuum is now established gradually, the sodium carbonate solution added by way of the smaller burette, and the distillation started and continued until 200 cc. have been distilled over, which is then nesslerized for free ammonia.

The vacuum tube is now disengaged and the stop-cock on large burette opened and about 250 cc. of the liquid in the distillation flask drawn up and the fifty cc. of alkaline permanganate solution, previously poured into the smaller tube, is now allowed to run in after the distillate flask has again been attached.

<sup>1</sup> Richards is an excellent device, but it is important to have a small check-valve in the tube to prevent the water being drawn into the apparatus when the water pressure is suddenly diminished. A very simple valve is made of oiled silk opening only toward the pump.

We now have fifty cc. of alkaline permanganate acting on fifty cc. of water, and after, say thirty to forty cc. have been distilled over, the water in the large tube is allowed to drop in at the same rate as the distillation, which must not exceed fifty cc. in fifteen minutes. [The rate of distillation, as recommended by the Chemical Section of the American Association for the Advancement of Science, *i. e.*, fifty cc. in ten minutes, is too rapid, and is very frequently accompanied by loss by imperfect condensation; this is very readily observed in my apparatus by discoloration of the Nessler solution in bulb.] The distillation is continued until 250 to 300 cc. have been distilled over, which is then nesslerized.

The following notes from my laboratory work will show the general plan of the work :

One gram urea was *dissolved in one liter* ammonia-free water.

1. Ten mgms. urea in 300 cc. of ammonia-free water, 250 cc. drawn up into tube, fifty cc. permanganate solution added, bath  $87^{\circ}\text{C}$ ., cooling water  $28^{\circ}\text{C}$ ., pressure six and a half inches, distillation at rate of 150 cc. per hour, 310 cc. distilled over with slight discoloration of Nessler bulb.  $30.2 : 2.0 :: 310 : 2.053$  mgms. ammonia, or 20.53 per cent. which is 36.2 per cent. on ammonia obtainable.

2. Five mgms. urea in 300 cc. ammonia-free water treated as above—297.4 cc. distilled over, no discoloration of Nessler bulb.  $28.8 : 1.0 :: 297.4 : 1.032$  mgms. ammonia, or 20.64 per cent. which is 36.4 per cent. on ammonia obtainable.

3. Ten mgms. urea in 300 cc. water, 250 drawn up, fifty cc. permanganate solution added, bath  $85^{\circ}\text{C}$ ., cooling water  $27^{\circ}\text{C}$ ., pressure five inches, rate of distillation, 100 cc. per hour, 290 cc. distilled over, no discoloration of Nessler bulb.

$25.1 : 2.0 :: 290.0 : 2.310$  mgms. ammonia, or 23.10 per cent. on 40.7 per cent. on ammonia obtainable.

4. Ten mgms. urea in 500 cc. water, ten cc. strong solution sodium carbonate added, bath  $87^{\circ}\text{C}$ ., cooling water  $28^{\circ}\text{C}$ ., pressure five and a half inches.

210 cc. distilled over as free ammonia, which yielded 0.835 mgms. ammonia or 8.35 per cent.

250 cc. were then drawn up, fifty cc. permanganate solution added, and distilled as before.

305 cc. were distilled over, which yielded 2.296 mgms. ammonia, or 22.96 per cent.

Total ammonia 8.35 per cent. free, plus 22.96 per cent. albuminoid, or 31.31 per cent. which is 55.2 per cent. on ammonia obtainable.

Rosaniline hydrochlorate yielded 86.02 per cent. on ammonia obtainable.

Strychnine sulphate	"	78.10	"	"	"	"
Urea-boiling five hours	"	79.90	"	"	"	"
Cyanuric acid	"	61.10	"	"	"	"
Quinine sulphate	"	77.09	"	"	"	"
Morphine sulphate	"	81.11	"	"	"	"

The apparatus, Fig. 1, is also used for the Kjeldahl process. This process was first described for use in general water analysis by Drown and Martin,<sup>1</sup> and is now very generally used in place of the Wanklyn process.

I have modified the Kjeldahl process so as to insure more perfect decomposition, and have obtained most gratifying results with the most obstinate organic compounds.

*Process.*—300 cc. of the water under examination is put into the distillation flask of apparatus already described (Fig. 1) and the whole connected up; ten cc. specially prepared concentrated sulphuric acid is allowed to drop in slowly by way of the smaller burette, the whole is then allowed to digest at 85° C., under diminished pressure for, say one hour, and then brought to a boil, and so continued until the contents are colorless. The acid is then neutralized and the solution rendered strongly alkaline by the addition of fifty cc. strong solution of ammonia-free, sodium hydroxide through the smaller tube.

250 cc. of the contents are then drawn up into the larger tube and fifty cc. of permanganate solution added through the smaller tube, and the distillation carried on as already described in the modifications of the Wanklyn process, and nesslerized as before.

The modified process combines the good features of the Wanklyn and Kjeldahl, and is easily carried out with the apparatus described. The original sources of error are now practically eliminated.

The following are some results upon some of the substances

<sup>1</sup> Technology Quarterly, 2, 3.

that with the Wanklyn process yield only a very small percentage of the ammonia. I have made no comparative tests with the original Wanklyn process, and quote Mallet's:<sup>1</sup>

	Mine.	Mallett, by Wanklyn's Process.			
Rosaniline hydrochlorate	96.9 per cent.	23.8	per cent	of theoretical amount.	
<sup>2</sup> Cyanuric acid					
(distillation two hours)	89.1	2.1	"	"	"
Cyanuric acid					
(distillation four hours)	91.2	"	"	"	"
Urea (from urine).....	100.3	22.2	"	"	"
Urea (from ammonium					
cyanate).....	99.0	20.8	"	"	"
Potassium ferrocyanide	59.8	none	"	"	"

In nesslerizing I have found the Leed's Comparator modified as in Fig. 2, best suited to my wants. The work is very much facilitated by having one tube with stop-cock carefully graduated up to 100 cc., and connected to another tube, as shown in Fig. 2 ;

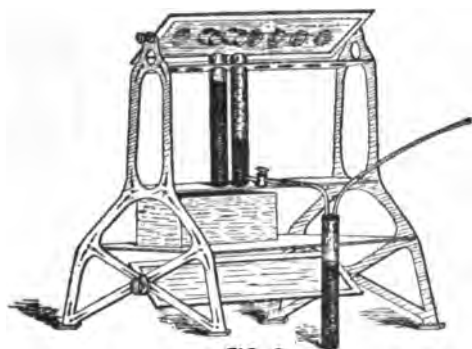


FIG. 2.

by using the blowing tube the liquid can be raised or lowered at will, and compared with the known solution with a nicety and exactness that I have been unable to attain by any other plan.

*Combustion Process.*—The Frankland combustion process<sup>3</sup> is entitled to more general use for regular work on water analysis; in my hands it has yielded satisfactory results after eliminating the objectionable features of open-air evaporation.

<sup>1</sup> Report Board of Health, page 253-254.

<sup>2</sup> After standing over night yielded 1.7 per cent. additional.

<sup>3</sup> Frankland: Water Analysis, London, 1890.

The apparatus designed for this purpose is shown in Fig. 3, and is constructed to hold a vacuum of fifteen mm. for four hours after pump has been stopped. The vessel A is set into a fixed table water-bath, to a depth of two inches, and the water under examination, in closed reservoir, B, the capacity of which is 200 cc., is admitted into A by a tube of very fine bore, and the vapor of water carried over into the sulphuric acid absorption col-

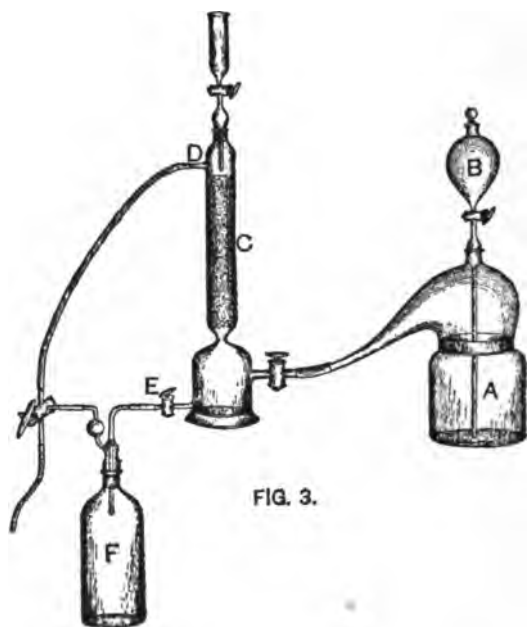


FIG. 3.

umn C, which is filled with broken glass tubing and has traveling through it, pure concentrated sulphuric acid. The vacuum tube to jet-pump is connected to the upper, D, and lower, E, connection of the absorption column by a three-way cock, by which the operation is momentarily suspended and the vacuum held, while the acid accumulated in the lower part of the column is drawn into a bottle, F, by diminished pressure.

Concentrated sulphuric acid is such a powerful absorbent that under the vacuum produced by a good jet-pump, ice can be readily and rapidly formed in the vessel, so that with the water in the bath at  $30^{\circ}$  C., the evaporation is rapid; actual boiling,



however, must not be permitted. The water is admitted only at the rate of evaporation which can be adjusted to a nicety by the stop-cock. Care must be taken to start the pump cautiously, thereby establishing the vacuum gradually, and to have only a thin layer of water in the vessel to avoid serious spattering in the escape of the bubbles of gas. In this way 500 cc. of water is evaporated to dryness in six to seven hours, and requires little or no attention after the apparatus is once adjusted.

The following comparative experiments have been made on water:

PARTS PER MILLION.				
	Wanklyn.	Wanklyn with my modifications and apparatus.	Kjeldahl, Drown, and Martin.	Kjeldahl with my modifications and apparatus.
	Free and albuminoid ammonia.		Organic nitrogen calculated as ammonia.	
Savannah river at } Augusta .....	Free, 0.011 Albu., 0.130	Free, 0.010 Albu., 0.165	0.172	0.175
	0.141	0.175		
Savannah river, at } 26 feet.....	Free, 0.180 Albu., 0.135	Free, 0.183 Albu., 0.236	0.421	0.420
	0.315	0.419		
Well water, Sum- } merville.....	Free, 0.092 Albu., 0.116	Free, 0.105 Albu., 0.186	0.285	0.287
	0.208	0.291		
Spring water sup- } plying Hotel Bon } Air .....	Free, 0.015 Albu., 0.123	Free, 0.018 Albu., 0.209	0.205	0.219
	0.138	0.227		
Driven well, be- } low Augusta...	Free, 0.685 Albu., 0.605	Free, 0.700 Albu., 0.976	1.855	1.867
	1.290	1.676		
Driven well in So. } Carolina.....	Free, 0.416 Albu., 0.395	Free, 0.422 Albu., 0.566	1.116	1.121
	0.811	0.988		
Artesian well } water, Georgia } Chem. Works..	Free, 0.005 Albu., 0.036	Free, 0.005 Albu., 0.042	0.050	0.050
	0.041	0.047		
Distilled water } with 10 per cent. } of water from pool } in garbage pile..	Free, 0.620 Albu., 1.136	Free, 0.653 Albu., 2.251	3.007	3.100
	1.756	2.974		

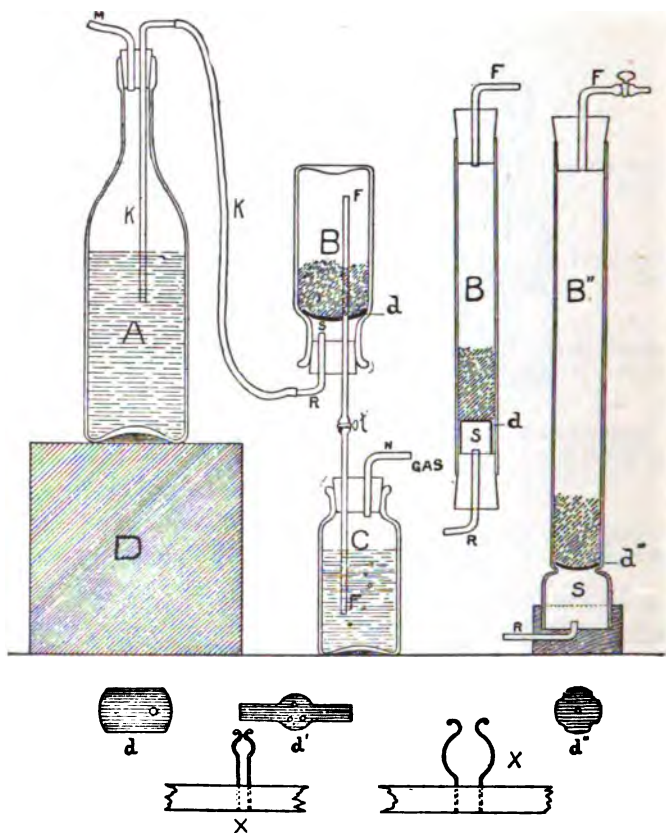
AUGUSTA, GA., December, 1894.

## A CHEAP FORM OF SELF-REGULATING GAS GENERATOR.

BY W. W. ANDREWS.

Received February 6, 1895.

**T**HIS form of generator is so cheap and easily set up that it makes it possible for every teacher and experimenter in chemistry to have, at practically no expense, a set of generators



capable of yielding, whenever called upon, a supply of hydrogen, hydrogen sulphide, chlorine, carbon dioxide, sulphur dioxide, etc. It consists of an ordinary bottle, A, to serve as reservoir

for the acid, a smaller bottle, B, which is the generator proper, and C, the familiar wash-bottle. A is closed by a cork holding two pieces of glass tubing. The one *m* just pierces the cork and the other, *k*, reaches down a short distance below the surface of the acid and is connected by means of a rubber tube with *r*, thus forming a siphon leading from A to B, as shown in cut. The tube *m* is used to start the siphon *kr* by blowing into A while the stop-cock, *l* is open. *f* is the exit tube for the gas. The charge of solid in B rests on a shelf of sheet lead, *d*, the width of which equals the diameter of the neck of the bottle, and its length the internal diameter of the bottle. It serves the purpose of securing a space, *s*, which prevents the extra gas generated, when *l* is closed, from pressing the acid out of the siphon. Instead of a bottle for holding the charge a calcium chloride tube, or an Argand lamp chimney, with its larger end closed with a cork or sunk into a wooden block and cemented with paraffin wax, or even a piece of large-sized tubing may be used. If the last be used the space *s* is secured by cutting the lead in the shape *d'* and bending it to form a bench to support the solid charge, as shown. *d''* is the shape of the lead support to be used in the calcium chloride tube or Argand chimney. *x* and *x'*, are the wire springs for holding B to its support, from which it may be lifted or replaced instantly. One is to enclose the body and the other the neck of the bottle, or one of the glass tubes below the cork.

The advantages of this form of generator are:

1. Its cheapness. An ordinary fruit-juice bottle and two wide-mouthed eight-ounce bottles will, with the necessary tubing, make one of good capacity.
2. Its convenience and safety. It is strictly self-regulating. If a rubber tube fitted with a glass plug one-half inch long, instead of a stop-cock be used, the gas flows only when the fingers pinch up the rubber along one side of the plug and ceases the moment they are lifted. The apparatus, therefore, is self-closing. It is very easy to recharge either with acid or solid.
3. It ensures a more even quality of gas than the well-known Kipp, and as complete utilization of the acid as the Koninck generator. When the gas presses the acid back from B, it enters A laden with dissolved solid and, on account of its greater specific gravity,

it falls in a straight line to the bottom, where it spreads out in a dense layer. When the apparatus is again set working, the purest acid is drawn from the upper layers. There is, consequently, some advantage in using a tall bottle for A.

4. It may be put together in a form which has all the advantages possessed by the Schanche generator (see this JOURNAL, Dec. 1894.) Making the glass tube R, long enough to reach to the top of B, and to curve a little downward, so that the acid may drop on the top of the solid charge and trickle through it. A drainage-tube with stop-cock must be inserted into the cork to carry off the used-up acid from the space S. The inverted bottle for B, possesses this advantage over the calcium chloride tube or chimney; *viz.*, that owing to the position of the mouth of the gas exit tube F, solid particles are not so likely to be shot into it when the acid is vigorously attacking the solid charge.

5. The pressure can be regulated at will by placing A at different heights, and this pressure may, at any moment, be reinforced by blowing into A, and the reinforcement held by closing M by means of a rubber tube and pinch-cock.

---

### SOME OF THE PROPERTIES OF CALCIUM CARBIDE.

BY F. P. VENABLE AND THOMAS CLARKE.

Received February 7, 1895.

THE calcium carbide used was prepared by the Willson Aluminum Company. In this preparation, lime is mixed with some form of carbon, as coal-tar; the mass is then heated, with stirring, until a thorough mixture is obtained. The proportions are so arranged that the mass becomes dry and hard on cooling. This mass, in lumps, is then placed in the electric furnace. In a very short time after the turning on of the current, the process is complete. The molten mass can be run out of the crucible or it may be removed after cooling. On examination, it is easy to see that there is more or less of carbon unchanged, or rather converted into the graphitic variety by the intense heat. Along with this are to be seen crystalline masses, lustrous and dark brownish black in color.

These are quite hard, and break with a crystalline fracture. Several efforts at effecting a separation from the graphitic carbon

were unsuccessful. The luster is slowly lost on exposure to air, more rapidly if the air be filled with moisture. The whole will finally crumble down into a gray powder with particles of black graphite interspersed through it. The carbide can be kept for a year or two if placed in a tightly stoppered bottle and is quite easily preserved if a little coal-oil is placed in the vessel containing it.

By far the most interesting property of this carbide is its decomposition when brought in contact with water. The metallic carbides seem to be distinguished by the ease with which they exchange their carbon for the oxygen of water or for the radicals of various acids, the carbon combining with the hydrogen to form various hydrocarbons. Several authors have reported that the decomposition of this particular hydrocarbon caused the formation of acetylene. Experiments were carried out by us proving this fact, some time before there were any publications concerning it in the chemical journals, but we were not at liberty to publish anything concerning it at that time. If the gas, as evolved, is passed through a set of absorption flasks containing ammoniacal copper solution it will be entirely absorbed, not a bubble passing through, out of one or two liters of the gas. Thus it seems to be pure acetylene. The amount of gas yielded by any one sample will be affected to some extent by the amount of graphitic carbon present. Hence different lots will vary somewhat. The average is about 200 cc. to the gram of carbide.

If the gas be ignited as it is evolved it gives a smoky flame; if it be considerably diluted, as one part of gas to from six to ten of air, a flame of great brilliancy and intensity is gotten. A company has been formed to introduce this as an illuminant upon the market. The cheapness of the materials used and the ease with which the gas can be formed ought to make it a valuable and useful addition to our illuminants. If too large a proportion of air be admixed a very violent explosion can be brought about by igniting it. In some cases we have noticed the flame rapidly travelling backwards along a rubber tube towards the gasometer in which the gas was stored. One explosion taught us that care was necessary in handling the mixture.

Several analyses were attempted of the carbide, but for obvious

reasons failed to give very satisfactory results. In the first place there was uncombined carbon present, also a small portion of a tarry matter which could be detected by heating to high temperatures, and lastly, the specimens worked upon were several months old and in spite of careful keeping, had been slightly acted upon by the air and so contained uncombined lime or calcium carbonate. Moissan gives  $C_2Ca$  as the formula calculated from his analyses. This would agree well with the decomposition by water;  $C_2Ca + H_2O = C_2H_2 + CaO$ .

*Action of Hydrogen upon the Carbide.*—Dry hydrogen has no action upon this carbide in the cold. Several small pieces of the carbide were placed in a piece of combustion tubing, drawn out at one end to a point suitable for testing the flame. Dry hydrogen was then passed over it and as soon as the air was expelled the hydrogen was ignited at the jet and a lamp placed under the tube so as to heat the carbide. In a little while the colorless flame became luminous and remained so a short time. A brownish tarry matter condensed in the cooler parts of the tube. The mass of the carbide assumed a dull gray tint and a very thin white sublimate collected at a short distance from where the tube was heated. The ignition was carried on for five hours. The driving off of this tarry matter seemed to be the only action. The substance on removal from the tube, was still hard. On exposure to the air, it disintegrated, and, if thrown into water, it was decomposed, showing the same behavior as the original carbide.

*Action of Air and of Oxygen.*—Some fresh pieces of the carbide were placed in the tube and heated while dry air was passed over them. A luminous flame was gotten as before and the same tarry matter was driven off and then there seemed to be no further action. Tests showed the carbide apparently unchanged at the end of prolonged heating.

Oxygen was then passed over some of the carbide which was being moderately ignited. No change was observed after two hours' heating. If the temperature was very high, such as that gotten in a combustion furnace, the carbide glowed brightly, as if burning, and a nearly white powder was obtained. The combustion was imperfect, however, unless the tube was very hot and the ignition prolonged. This refers not merely to the gra-

phitic carbon mixed with the carbide but to the carbide itself. In several experiments the substance withdrawn from the tube, after heating some hours in oxygen, decomposed violently in water. It may be added, as was to be expected, that carbon dioxide had no appreciable action upon the carbide.

*Action of Hydrochloric Acid.*—Hydrochloric acid had no action upon this substance in the cold. When passed over the heated substance it caused it to swell up and assume a dirty gray appearance. A small amount of a liquid, apparently water, collected in the cooler portions of the tube and parts of the carbide fused down in glassy globules and masses. These were soluble in water and were easily shown to be calcium chloride. White fumes were evolved some of which settled as a white solid upon the sides of the tube.

*Action of Chlorine and Bromine.*—When chlorine was passed over fresh carbide in the cold no action was observed. If even a moderate heat was applied, however, the lumps of carbide glowed very brightly, swelled, and fused together. A slight yellowish white sublimate was found in the tube. The fused mass was calcium carbide.

Bromine mixed with air was then passed over the fresh carbide. In the cold no action was observed. On heating, the carbide became red and the smaller pieces glowed. The lumps fused together and bubbles were observed on the surface as if some gas was escaping from the mass. Some condensed matter was found afterwards in the tube, and, on cooling, a peculiar odor was noticed different from that of bromine. The fused mass dissolved readily in water and gave the tests for calcium bromide. Of course in this and the previous experiment the black specks of graphitic carbon were found unchanged. It was easy to distinguish them from the carbide. A few pieces of the carbide were dropped into strong, freshly prepared, chlorine water. There was a very violent disengagement of gas but it was not ignited as reported by Moissan. The gas was inflammable and burnt very much like acetylene. The odor was, however, peculiar. The same experiment was tried several times with a concentrated solution of bromine in water. The action again was very violent but there was no spontaneous ignition of the gas.

Little difference could be detected between this and the action of the chlorine water.

*Action of Acids.*—A piece of the carbide was placed in concentrated pure sulphuric acid. A few small bubbles came off but the action seemed slight. On heating, the action was greatly increased and continued after the removal of the flame. A gas was given off which burned with a luminous flame.

A mixture of sulphuric acid and potassium bichromate acted most violently upon the carbide. There seemed to be a very vigorous oxidation, and several attempts at igniting the gas given off resulted in failure. There could have been very little, if any, acetylene present in it.

Strong nitric acid attacked the carbide with the formation of brown-red fumes. The gas evolved could be ignited and burned with a smoky flame.

Glacial acetic acid decomposed the carbide slowly in the cold.

It may be added that no change was observed on adding a piece of the carbide to some boiling sulphur. On allowing the mass to cool the carbide was regained in its original condition.

*Action of Alkalies.*—A few grams of sodium hydroxide were melted in a nickel dish and a piece of the carbide was added. There was violent action, a gas being given off which burned with a luminous flame and which was taken to be acetylene.

A small amount of sodium dioxide was also melted in a nickel dish. When the carbide was added to this it was rapidly attacked, the action being about the same as in the experiment just mentioned. An inflammable gas was evolved.

In conclusion, we would give due credit to Mr. W. R. Kenan, who carefully verified some of the experiments here recorded.

UNIVERSITY OF NORTH CAROLINA,  
February, 1893.

---

### NOTE ON THE DETERMINATION OF ZINC.

BY P. W. SHIMER, EASTON, PA.

Received January 24, 1895.

THE manganese in many zinc ores is a disturbing element in the accurate determination of metallic zinc. As is well known the usual separation of zinc from manganese is made by precipitating the zinc as sulphide in a solution which is strongly



acidified with acetic acid. When the manganese is high this precipitate should be dissolved and reprecipitated to purify the zinc sulphide from a little manganese sulphide thrown down with it. To avoid this troublesome reprecipitation I have lately used the following method which does away with the disturbing influence of manganese, and gives results agreeing closely with those obtained by the usual methods.

About eight-tenths gram of the zinc ore is dissolved as usual in hydrochloric acid. In case, as often occurs, there is any insoluble manganese or zinc spinel in the residue, it is necessary to make a fusion. Evaporate the hydrochloric solution to dryness and redissolve and filter if it is desired to determine the silica. In case silica is not to be determined it need not be filtered off. Redissolve in nitric acid (1.20) and evaporate to moist dryness. Add 100 cc. strong nitric acid and precipitate the manganese as dioxide by means of potassium chlorate, as in Ford's method for manganese in iron and steel. Filter through purified asbestos by means of the filter-pump and wash, first with strong nitric acid, then with cold water. Dissolve the manganese precipitate in standardized ferrous sulphate solution and titrate the excess of ferrous sulphate with standardized permanganate solution as in Williams' method for manganese in iron and steel. In this way the manganese is promptly separated, and if desired, determined.

The filtrate from manganese is transferred to a beaker and evaporated to dryness. A little hydrochloric acid is added and again evaporated to moist dryness. On this solution the usual double basic acetate precipitation is made. The united filtrates are evaporated to a bulk of about 300 cc., heated to boiling, removed from the flame, and a rapid current of hydrogen sulphide passed through for one-half hour. The zinc sulphide is filtered off and dissolved in hydrochloric acid and the zinc precipitated, preferably as zinc ammonium phosphate. The precipitate is separated from the paper and weighed as zinc pyrophosphate. The ignition should be done cautiously at a low red heat to avoid fusion of the pyrophosphate and a probable cracking of the crucible at the moment of solidification. In case lime is to be determined in the filtrate from the zinc sulphide, it is

necessary to dissolve and reprecipitate the calcium oxalate, for the first precipitate is sure to contain alkaline chlorides in very appreciable amount. The basic acetate precipitate cannot be used for the determination of alumina, since the manganese precipitate carries down a little iron with it, but apparently no determinable amount of zinc.

### ON THE DETERMINATION OF CANE-SUGAR IN THE PRESENCE OF COMMERCIAL GLUCOSE.<sup>1</sup>

BY H. A. WEBER AND WILLIAM MCPHERSON.

IN the analysis of a great many of the saccharine products found in the markets at the present time, the chemist is confronted with the problem of determining sucrose in the presence of commercial glucose. The official methods for such determinations, either by the use of Fehling's solution alone or supplemented by the polariscope, necessitate, as is well known, the inversion of the sucrose by the action of acids. The accuracy of these methods requires, as one condition, that the acid used in inversion exert no action upon any substance present, other than sucrose, that would in any way affect the reading of the polariscope or would change the power to reduce Fehling's solution. Since commercial glucose, however, contains a greater or less amount of dextrin, and since this undergoes hydrolysis when acted upon by acids, being changed thereby into dextrose, the question arose as to whether such a change might take place during the process of inversion of any sucrose present and thus vitiate the results. The specific rotatory power of dextrin being nearly four times as great as that of dextrose, it is evident that a very slight action would introduce serious errors.

The method of procedure was, first, to determine to what extent dextrin is present in commercial glucose; second, to ascertain whether any change is produced by heating with acids as in the common process of inversion, and finally to discover some method of eliminating this error, if present.

<sup>1</sup> This paper and the one following were sent to Dr. H. W. Wiley to be read before the Association of Official Agricultural Chemists and then transmitted to the editor of this JOURNAL for publication. In consequence of a misunderstanding they were printed instead, in the Proceedings of the Eleventh Annual Convention of the above association. At the request of the authors, and with the consent of the Committee on Papers and Publications, they are now reprinted in full.—ED.

An examination of the literature accessible upon the subject of the composition of American glucose failed to give any information in regard to the amount of dextrin present.

The report on glucose, Washington, 1884, gives the analysis of some glucoses, but as suggested by Stone and Dickson,<sup>1</sup> improvement or variation in the manufacture since that time would probably cause a change in the chemical composition.

In order to obtain the desired information a number of samples were analyzed. Seven of the samples were kindly sent us by the American Sugar Refining Company, of Chicago, and represent the various grades placed on the market by them. Since this company controls the glucose manufacture in the United States, it is fair to presume that these samples represent, more or less fairly, an average glucose in the market. Two other samples were purchased in Columbus, but analysis showed a composition similar to those sent from Chicago, and inquiry revealed the fact that they had been purchased from the above-mentioned company.

#### METHOD OF ANALYSIS.

A number of different methods have been proposed for the estimation of the constituents of glucose, all more or less objectionable. The shorter ones are only fairly approximate, making no attempt to estimate the amount of the so-called inert or unfermentable carbohydrates (gallisin). The longer methods are probably more exact, but, since the unfermentable carbohydrates are but imperfectly known, it follows that any attempt at finding the exact composition cannot be highly satisfactory.

The following method<sup>2</sup> was selected as giving approximately the relative amounts of dextrose, maltose, and dextrin present.

Twenty-five grams of the glucose were dissolved in water, and the solution made up to 250 cc. With this solution the following determinations were made:

1. *Specific gravity*.—This was determined by weighing with the pyknometer. The Westphal balance was first used, but the results were not so satisfactory as those obtained by direct weighing.

2. *Specific rotatory power*.—This was deduced from the direct

<sup>1</sup> *J. Anal. Appl. Chem.*, 7, No. 6.

<sup>2</sup> See article Sugar, Thorpe's Dictionary of Applied Chemistry.

reading in a 200 mm. tube. The instrument used was the ordinary Schmidt and Haensch polariscope. Its accuracy was tested by a standard plate, kindly loaned by Dr. Wiley.

3. *Cupric reducing power*.—A gravimetric determination was made by adding ten cc. of the solution properly diluted to forty cc. of Fehling's solution previously heated in boiling water until it attained a like temperature and then heating for twelve minutes in water at 100°. The cuprous oxide was filtered through asbestos, well washed, and changed into the cupric form by igniting for fifteen minutes. The weight of the oxide multiplied by 0.4535 gives the amount of reducing sugar present. Experiment showed that good results could be obtained by exercising due care and adhering rigidly to the conditions.

4. *Ash*.—Fifty cc. of the solution were treated with sulphuric acid in a platinum dish until all the carbonaceous matter was burned away, the residue weighed, and the percentage of ash calculated.

The total organic solid matters per 100 cc. were determined by subtracting from the specific gravity of the solution (water = 1,000) the correction due to the ash, and dividing the difference between the result and 1,000 by 3.86. This is based on the assumption that ten grams of carbohydrates dissolved in 100 cc. of water give a solution of sp. gr. 1,038.6 (water = 1,000), also that one gram of ash per 100 cc. gives a specific gravity of 1,008. Now, if in a solution containing ten grams to 100 cc.,

S = total carbohydrates,

(A)d = specific rotatory power for ray D,

K = cupric reducing power in terms of dextrose,

then

$$\text{Maltose (M)} = \left( \frac{(A)d + 1.42K - 195}{27.2} \right) S$$

$$\text{Dextrose (D)} = \frac{SK}{100} - 0.61 M.$$

$$\text{Dextrin} = S - (M + D).$$

It is evident that this method will give only approximate results, since it supposes that the only organic bodies present are maltose, dextrose, and dextrin. However, the results undoubtedly give a fair insight into the amounts of these present.

TABLE NO. I.—GLUCOSES ANALYZED.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Specific gravity.....	1030.60	1031.05	1031.40	1031.18	1033.16
Total solids, grams .....	7.8890	8.01	8.08	8.03	8.56
Specific rotatory power .....	133.33	132.90	120.60	135.40	132.10
Ash, per cent.....	0.18	0.19	0.24	0.21	0.17
Cupric reducing power, per ct.	56.56	57.00	60.60	54.90	56.70
Maltose, per cent .....	54.08	55.44	34.63	54.20	55.40
Dextrose, per cent.....	11.64	11.81	21.24	11.03	14.71
Dextrin, per cent.....	13.18	12.80	24.98	15.09	15.44
	No. 6.	No. 7.	No. 8.	No. 9.	No. 10.
Specific gravity.....	1033.90	1031.17	1031.48	1033.50	.....
Total solids, grams .....	8.74	8.00	8.11	8.60	.....
Specific rotatory power .....	127.80	149.30	130.31	134.91	40.20
Ash, per cent.....	0.22	0.37	0.29	0.37	.....
Cupric reducing power, per ct.	55.90	43.60	50.65	48.75	.....
Maltose, per cent .....	39.12	47.67	22.30	28.92	.....
Dextrose, per cent .....	25.08	5.81	27.48	24.31	.....
Dextrin, per cent .....	23.18	26.52	31.33	32.81	.....

It is of interest to compare these results with the following, the first three of which are taken from the report on glucose above mentioned. The fourth is the analysis published recently of a product manufactured in England.

	No. 1. Per cent.	No. 2. Per cent.	No. 3. Per cent.	No. 4. Per cent.
Maltose .....	19.3	7.6	....	36.10
Dextrose ....	36.5	36.5	39.0	18.75
Dextrin .....	29.8	40.9	41.4	25.41

The most noticeable feature of the above analyses is the high per cent. of maltose present and the comparatively low per cent. of dextrose. With a single exception the maltose present exceeds the dextrose, reaching a maximum difference in number 7, which contains 47.67 per cent. maltose and only 5.81 per cent. of dextrose. This particular sample was labeled "Brewers' Extract," the name suggesting a high per cent. of maltose, a characteristic property of the glucoses obtained from Chicago with a malt-like odor noticeable when dissolved in a slight amount of hot water. It will be noticed that the English sample contains almost twice as much maltose as dextrose.

The solid glucose or grape-sugar was not analyzed completely, since the specific rotatory power was so low as to exclude any possibility of the presence of dextrin.

It is of interest to compare the properties of the above glucoses with those examined by Stone and Dickson.<sup>1</sup> The determinations made by them were, in the main, different from those made by us, overlapping, however, in the determination of the specific rotatory power and ash. A marked difference exists in these. The average specific rotatory power of those examined by Stone and Dickson is given as 91.37, while those examined by us showed a variation from 120.6 to 149.3, calculated for ray D. It is possible that the former calculations may have been made for some other ray, and the apparent difference thus diminished. The percentage of ash in the samples examined by us was noticeably smaller, being about one-fourth as great.

The glucoses were next subjected to the same treatment as would be necessary to invert sucrose, if present, *viz.*, heating with acids. It is evident that in order to guard against any hydrolysis of the dextrin or to diminish it, if unavoidable, the temperature to which the acid solution is raised as well as the time during which this temperature is maintained should be no greater than necessary to insure complete inversion of the sucrose. Various methods of inversion have been proposed and various ones are in use by chemists at the present time. The official methods of the agricultural chemists for the years 1890 and 1891 require that the solution to be inverted, mixed with the proper amount of acid, be heated for ten minutes at 68°. This was changed in the report for 1892 and continued in the report for 1893, to heating gradually, reaching 68° at the expiration of ten minutes. This is also the method given by Allen,<sup>2</sup> as well as the one recommended by the "Association des Chimistes."<sup>3</sup>

Three different methods were tried: 1. The above-mentioned or official method; 2. The method recommended by the Association of Official Agricultural Chemists for the years 1890 and 1891, *viz.*, heating at 68° for ten minutes; 3. The German method, which amounts to heating at 67° to 70° for fifteen minutes.

Approximately 26.048 grams of glucose were dissolved in 200 cc. of water. Fifty cc. of this solution mixed with five cc. fuming

<sup>1</sup>*J. Anal. Appl. Chem.*, 7, No. 6.

<sup>2</sup>Allen's Commercial Organic Analysis.

<sup>3</sup>*Jour. des Fabr. de Sucre*, 32, 1897, No. 35.

hydrochloric acid were heated according to the above-mentioned methods.

TABLE NO. II.—READINGS OF AN APPROXIMATELY FIFTY PER CENT. SOLUTION OF THE VARIOUS GLUCOSES, BEFORE AND AFTER HEATING WITH ACIDS. TEMPERATURE, 20° C.

[Divisions on cane-sugar scale.]

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.	No. 9.	No. 10.
Direct reading										
200 mm. tube	85.70	85.50	80.10	86.55	85.30	84.40	90.40	84.90	86.15	42.00
Reading after inversion by										
first method	85.20	84.85	79.58	86.00	84.90	83.90	89.85	84.20	85.55	42.05
Difference	0.50	0.65	0.52	0.55	0.40	0.50	0.55	0.70	0.60	....
Reading after inversion by second method										
.....	84.25	83.90	78.75	85.15	84.00	82.90	88.95	83.00	84.45	....
Difference	1.45	1.60	1.35	1.40	1.30	1.50	1.45	1.90	1.70	....
Reading after inversion by third method										
.....	83.75	83.20	78.10	84.60	83.50	82.15	88.35	82.25	83.75	....
Difference	1.95	2.30	2.00	1.95	1.80	2.25	2.05	2.65	2.40	....
Reading after boiling one hour with acetic acid (com.)										
.....	85.30	84.90	79.75	86.15	84.85	84.05	89.90	84.30	85.65	....
Difference	0.40	0.60	0.35	0.40	0.45	0.35	0.50	0.60	0.50	....

The flasks were carefully calibrated and the duplicates agreed within the error of reading. The results are given in the above table. The solutions were of such a strength that the amount used was the same as would be used in the analysis of a substance containing approximately fifty per cent. glucose.

It will be noticed that in every case, with the exception of No. 10, which contains no dextrin, the reading is sensibly diminished, introducing thereby an error in the estimation of sucrose in the presence of commercial glucose, varying from one-tenth to over two per cent., according to the amounts of the two present and the method of inversion used. While this may not be large enough to cause one to draw unjust conclusions from the analysis of commercial saccharin products, it is nevertheless desirable to eliminate it if possible, or at least to reduce it to a minimum.

Experiments were made to find out the effects of other acids in the hope of finding one that would bring about the inversion without affecting the reading of the glucose. The result showed, however, that even an acid which would not bring about complete inversion would sensibly diminish the reading of the glucose. Thus acetic acid will cause a diminution of reading almost as large as that caused by hydrochloric acid, although it does not *seem* to cause complete inversion. In no case was a smaller error introduced than by the first method above used.

Since the error could not be eliminated by inversion with acids<sup>1</sup> an attempt was made to allow a correction for it. It is evident from the above results that the error is not a widely diverging one, if the samples can be regarded as average ones, and it could be largely diminished by allowing for the mean deviation.

It was necessary, however, before attempting this to find out what the effect would be when the amount of glucose present was varied. Solutions were made containing, approximately, 100, 50, 25, 10, and 5 per cent. of glucose, respectively, and subjected to the action of acids as before. The average results expressed as divisions on cane-sugar scale, were as follows :

	100 per cent.	50 per cent.	25 per cent.	10 per cent.	5 per cent.
Before.....	170.7	85.00	42.35	16.8	8.6
After.....	169.4	84.45	42.15	16.78	8.65
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	1.3	0.55	0.2	0.02	....

The results with the various glucoses are sufficiently uniform to warrant one to introduce corrections which, while not eliminating the error, would reduce it to a minimum.

This correction may be easily calculated as follows :

It can readily be seen that the reading due to glucose present may be approximately determined by subtracting from the direct reading three-fourths of the difference between (or sum of) the direct and invert readings (supposing that the temperature be about 20°).

<sup>1</sup> This error would be eliminated by the inversion brought about by O'Sullivan and Thompson's invertase process (*Journal of the Chemical Society of London*, 59, 46). The method is not used to any extent, however, because of the time required as well as the increased labor of analysis.



Let  $R$  equal the reading due to glucose, then the following formula deduced from a graphic representation of the above results will be found to give the correction ( $x$ ) :

$$x = \frac{R-15}{130}$$

This correction must, of course, be subtracted from the numerator ( $a \pm b$ ) in Clerget's formulas. In order to test the accuracy of the above correction a number of mixtures of cane-sugar and glucose were analyzed. Good results were obtained in every instance. The following expressed as divisions on cane-sugar scale, will serve as examples :

Glucose. Per cent.	Sucrose. Per cent.	Direct reading.	Invert reading.	Approximate glu- cose read- ing.	Correc- tion.	Per cent. of sucrose found	
						Without correction.	With correc- tion.
80	20	154.2	126.30	133	0.90	20.82	20.18
50	50	138.4	70.75	87	0.55	50.48	50.11
30	70	120.3	26.23	50	0.27	70.20	70.00
10	90	109.0	11.80	19	0.03	90.15	90.13

The results in Table No. 11 show the necessity of chemists using the same method of inversion. Even in the estimation of pure sucrose it has been shown by a number of chemists that the reading varies slightly according to the method used. In the presence of commercial glucose, however, the variation becomes much greater. When the inversion is accomplished by heating at  $68^{\circ}$  for ten minutes, the difference in reading due to the hydrolysis of the dextrin averages almost three times as great as when the first method is used, while the German method increases this to almost four times. It is barely possible that some of the widely varying results published by the reporter on sugar, in the report of the Association of Official Agricultural Chemists, may owe a part of their discrepancies to these facts.

#### CONCLUSIONS.

Some of the conclusions reached may be summarized as follows :

(1) An error is introduced in the estimation of sucrose in the presence of commercial glucose, due to a slight hydrolysis of the dextrin present during the process of inversion of the sucrose by acids.

(2) This hydrolysis, and consequently the error, is reduced to a minimum when the inversion of the sucrose present is effected by heating for ten minutes, the temperature being gradually raised so as to reach  $68^{\circ}$  at the expiration of this time.

(3) The results with the different glucoses are sufficiently uniform to warrant the introduction of a correction for the mean error.

(4) In order that the results may be comparable, chemists ought to strictly adhere to one method of inversion.

OHIO STATE UNIVERSITY,  
COLUMBUS, OHIO.

### ON THE ACTION OF ACETIC AND HYDROCHLORIC ACIDS ON SUCROSE.

BY H. A. WEBER AND WILLIAM MCPHERSON.

WHILE carrying out some experiments with glucose several facts were noted in reference to the action of acetic and hydrochloric acids on sucrose, which it is interesting to compare with the conclusions reached by Bornträger,<sup>1</sup> Jungfleisch and Grimbert,<sup>2</sup> and Ost.<sup>3</sup> Inasmuch as we were working with an entirely different object in view, the conclusions reached were in no way influenced by the conclusions reached by the above writers.

While making an examination of a large number of saccharine products, the writers were led to believe from certain results that complete inversion could be effected by means of acetic acid. This view was contrary to the general opinion of chemists, although as prominent ones as Jungfleisch and Grimbert<sup>4</sup> claim that acetic acid completely inverts sucrose at  $100^{\circ}$ , and that it is preferable to other acids, since its presence is without effect upon the levulose of invert sugar. This conclusion was reached from the fact that the specific rotatory power of pure levulose corresponded almost exactly with that of levulose calculated from invert sugar, the inversion being effected by acetic acid. Hydrochloric acid gives a higher invert reading, because, in some way, it acts upon the levulose and increases very percepti-

<sup>1</sup> Boh. Zeit. Zucker, Ind., 1897, 187. Bull. Assoc. Chim., 1892, 559.

<sup>2</sup> *Compt. rend.*, 107, 390, and 108, 144.

<sup>3</sup> *Ber. d. chem. Ges.*, 24, 1636.

<sup>4</sup> *Compt. rend.*, 107, 390.

bly, its specific rotatory power. Exceptions to this view are taken by Maumené,<sup>1</sup> who calls attention to the fact that the invert sugar prepared from sucrose by action of acids is not composed of equal parts of levulose and dextrose. Ost<sup>2</sup> not only denies that acetic acid will produce complete inversion, but also claims that it acts perceptibly upon invert sugar. Ross<sup>3</sup> states, as the result of a number of experiments, that it was found impossible to secure complete inversion even when ten per cent. glacial acid was used and the flask kept immersed in boiling water for forty-five minutes.

Those who claim that acetic acid does not effect complete inversion base their belief upon the fact that invert sugar, prepared by the action of hydrochloric acid upon sucrose, gives a higher reading than the corresponding solution obtained by the action of acetic acid. It was thought that perhaps acetic acid might form some compound with the constituents of the invert sugar, which might affect the reading of the polariscope. Proceeding upon this assumption, attempts were made to decompose such a compound. In the course of these experiments, which were conducted at great length, certain facts were noted which have been systematized in the following:

As stated above, Jungfleisch and Grimbert in particular, have called attention to the fact that the specific rotatory power of invert sugar, prepared by the action of hydrochloric acid on sucrose, is higher than that of the artificially made invert sugar. If, however, as Maumené claims, the invert sugar so prepared is not composed of equal parts of dextrose and levulose, then it is possible that the different readings are due to the peculiar compounds formed. In fact, one would not expect the readings to be identical under such assumptions.

Accordingly, experiments were undertaken to find out, if possible, whether the hydrochloric acid used in inversion affected in any way by its presence the reading of the invert sugar so prepared. Attempts were made in two different directions.

1. Five hundred cc. of a normal solution of sucrose (polariz-

<sup>1</sup> *Journal des Fabricants de Sucre*. Abstract from March 27, 1889.

<sup>2</sup> *Ber. d. chem. Ges.*, 24, 1636.

<sup>3</sup> Report of the Association of Official Agricultural Chemists, Bul. 35, Div. of Chem., Dept. Agr., p. 146.

ing at 99.8) was subjected to inversion in 100 cc. flasks by adding one-tenth the volume of concentrated hydrochloric acid (sp. gr. 1.19) and heating for ten minutes, regulating the heat so that the temperature, 68°, was reached at the end of that time. These solutions were all poured into a large flask and thoroughly mixed, so as to obtain a perfectly uniform solution. Exactly fifty-five cc. of this solution were transferred to a 100-110 cc. flask, the flask filled to the mark with water, the solution thoroughly mixed and polarized. The experiment was repeated with the addition of five cc. of the same acid used in the inversion, previous to filling to the mark with water; again repeated with the addition of ten cc., fifteen cc., and twenty cc., respectively. Since the same solutions, same flasks, and polarizing tubes were used, and the temperature of the solutions did not differ more than 0.5°, corrections being introduced for this variation the chances of error in manipulation were very slight. The following readings, expressed in divisions of cane-sugar scale, were obtained for the various solutions (temperature = 20°):

Invert sugar (containing five cc. of acid).....	— 33.00
Invert sugar + five cc. additional acid .....	— 33.90
Invert sugar + ten cc. additional acid.....	— 34.65
Invert sugar + fifteen cc. additional acid.....	— 35.60
Invert sugar + twenty cc. additional acid .....	— 36.40

The reading is seen to increase with the addition of the acid, thus agreeing with the conclusion of Gubbe.<sup>1</sup> Moreover, the deviations caused by the addition of the different amounts of acid are fairly constant, varying from 0.75 to 0.95, or an average of 0.85. It was hoped that sufficiently uniform results could be obtained to allow the graphic representation, so that an estimate could be made on the effect of the original five cc. of acid added to bring about inversion. Since, however, the addition of a second, third, fourth; and fifth five cc. of acid each increases the reading of the invert sugar approximately 0.85, then we may conclude, with some probability, that the original five cc. of acid which effected the inversion would increase the reading by that amount.

2. Attempts were also made to solve the problem by neutral-

<sup>1</sup> *Ber. d. chem. Ges.*, 18, 2207.

izing the acid present in the invert solution by the action of sodium carbonate.

Bornträger<sup>1</sup> has called attention to the fact that the rotatory power of the neutralized solution is higher than that of the corresponding acid solutions. By the addition of sodium carbonate, however, not only is the acid neutralized, but a corresponding amount of sodium chloride is thereby added. Readings were taken first to find out the effect of the addition of the sodium chloride. Then, by comparing this with the variation caused by neutralization with sodium carbonate, the effect of the acid could be deduced.

Five hundred cc. of inverted sugar solution were prepared as described above. It was found that three and three-tenths grams of pure dry sodium carbonate were necessary to neutralize the acid (five cc.) present in fifty-five cc. of this solution. The experiments were conducted as in the above. Fifty-five cc. of the solution were transferred to a (100-110) flask, neutralized with sodium carbonate, the flask filled to the mark, the solution mixed thoroughly and polarized. The duplicates agreed within the limit of error in reading. The average readings on cane-sugar scale were as follows (temperature = 20°):

	Triplicates.		
	1.	2.	3.
Original solution.....	-33.1	-33.0	-33.20
Original solution + 3.3 grams sodium carbonate (neutral).....	-33.7	-33.7	-33.85
Original solution + 6.6 grams sodium carbonate .....	-36.2	-36.0	-36.30

The last reading was taken in order to compare the effects of the addition of sodium carbonate before and after neutralization. It is thus seen that, while the reading of the normal solution is increased 0.6° by the addition of the necessary amount of carbonate to neutralize the acid, the subsequent addition of a like amount increases the reading 2.5°. Before ascribing this difference in reading to the effect of the acid, it is necessary to find whether or not the sodium chloride, formed by the addition of the sodium carbonate to hydrochloric acid, affected the reading.

Experiments were conducted with the same solution used

<sup>1</sup> Boh. Zeit. Zucker, Ind., 1891, 187.

above. Fifty-five cubic centimeters of the solution were introduced into the 100–110 cc. flask, and the amount of sodium chloride corresponding to three and three-tenths grams of sodium carbonate, or 3.65, added, the flask filled and the solution polarized as before. The average readings on cane-sugar scale, agreeing within  $0.1^\circ$ , are :

Original solution.....	—33.1	—33.15
Original solution + 3.65 grams sodium chloride..	—35.1	—35.10

Since, then, the effect of the sodium chloride was to increase the reading  $2^\circ$ , the acid remaining unneutralized, while the reading was only increased  $0.6^\circ$  by the addition of the same amount of sodium chloride, the acid being neutralized at the same time, the difference  $1.4^\circ$  may presumably be attributed to the action of the acid present.

This result is higher than the one deduced from the direct addition of acid given above, but it is undoubtedly the more correct of the two. It would thus seem that the acid undoubtedly increases the rotatory power, the probable increase of reading being about  $1.4^\circ$  on the direct scale for the normal solution.

Similar experiments were next conducted in order to find out the effect of acetic acid. The strength of the acid used may be inferred from the fact that five cc. of it required for neutralization 3.05 grams of dry sodium carbonate. The normal solution of sucrose was heated at  $100^\circ$  with one-tenth volume of this acid for about one hour, experiments showing that continued heating had but little effect upon the reading. By this treatment a reading for the normal solution was obtained on an average of  $2^\circ$  lower than when hydrochloric acid was used as the agent of inversion. The same solution which gave a reading of  $-33.1^\circ$  when hydrochloric acid was used gave a reading of  $-31.1^\circ$  when treated with acetic acid under the above conditions.

Experiments performed to discover whether the subsequent addition of acetic acid would affect the reading, gave the following results, on cane-sugar scale :

Original invert solution (temperature $20^\circ$ ).....	—31.10	—31.0
Original invert solution + ten cc. additional acetic acid...	—30.85	—30.8

The second reading is the reading obtained from a solution exactly the same as the first ten cc. of acetic acid being introduced.

It thus appears that while hydrochloric acid increases the reading by its presence, acetic acid decreases it by a small but perceptible amount. This result agrees with Ost, who criticises the statement of Jungfleisch and Grimbert that acetic acid has no effect upon invert sugar. In order to test this further, the acid was neutralized by sodium carbonate and the difference of reading noted. This result, united with the effect due to the introduction of the sodium acetate formed, gave the means of finding the effect of the acid.

The experiments were conducted as in the above, using same solution, same flasks, and same polarizing tubes. The following are the results obtained, on cane-sugar on scale :

Original solution (temperature 20°).....	—31.20	—31.1
Original solution + 3.05 grams sodium carbonate (neutral)	—32.65	—32.6
Original solution + (3.05 X 2) grams sodium carbonate..	—34.80	—34.8

A marked difference is noted here as compared with similar experiments with hydrochloric acid. The neutralization of the hydrochloric acid increased the reading only 0.6°, while the neutralization of the acetic acid increased the reading over twice the amount, or 1.5°. The subsequent effects of the sodium carbonate upon the two solutions agree very well, being an increase of 2.5° in the case of hydrochloric acid against an increase of 2.2° in the case of acetic acid. This difference of 0.3° in the reading is accounted for by the fact that 3.3 grams of sodium carbonate were added in the hydrochloric acid solution, while only 3.05 grams were added in the acetic acid solution. If correction be made for this difference, the increase in readings differ only by 0.1°.

It was necessary also to find out the effect of the sodium acetate formed by the neutralization of the acetic acid by sodium carbonate. The readings on the cane-sugar scale were as follows :

Original solution (temperature 20°).....	—31.1	—31.1
Original solution + 4.72 grams sodium acetate....	—32.4	—32.4

The sodium acetate used was the pure anhydrous salt.

It is thus seen that while the sodium carbonate increased the reading 1.5°, the introduction into the original solution of the same amount of sodium acetate as was formed increased the

reading but  $1.3^{\circ}$ . The difference of  $0.2^{\circ}$  must be due to the presence of the acid.

The conclusion that the acetic acid by its presence lowers slightly the reading is confirmed by the fact that by the use of a weaker acid a maximum reading of  $-31.3^{\circ}$  was obtained.

As might be expected the introduction of hydrochloric acid into a solution inverted by acetic acid increases the reading in a corresponding degree.

It is thus shown that the effect of hydrochloric acid upon a solution of invert sugar is to increase the reading, while acetic acid has an opposite effect. Moreover, the experiments show that the probable increase in reading due to hydrochloric acid under the conditions mentioned is  $1.4^{\circ}$ , while the probable decrease in reading due to acetic acid is  $0.2^{\circ}$ . In other words, if these two acids produced the same effects upon being heated with sucrose, there would still be a difference of reading of  $1.6^{\circ}$  due to the presence of the acid. This agrees fairly well with the actual difference observed.

In the light of these experiments it may be of interest to notice the question so often discussed, "Does acetic acid effect complete inversion?" If we suppose that no acid effects complete inversion unless it gives a reading such as that obtained by using hydrochloric acid, then most certainly acetic acid does not invert completely. If, on the other hand, we adopt as the reading of the invert solution the reading of the acid solution, corrected for the effect produced by the presence of the acid, then acetic acid gives more nearly the correct invert reading, and it is correct to affirm that acetic acid does invert sucrose completely.

Finally, the above results indicated that when Fehling's solution is used in the place of the polariscope, it would be a matter of indifference whether acetic or hydrochloric acid was used to effect the inversion of the sucrose. Experiments showed this to be true. Two solutions containing the same amount of sucrose were inverted with hydrochloric and acetic acids respectively. After inversion exactly 11.7 cc. of each solution were required to reduce ten cc. of Fehling's solution. Moreover, when Fehling's solution is used for the determination of sucrose in presence of dextrin or commercial glucose, acetic acid is preferable to hydro-



chloric acid as the agent of inversion, since the process requires no attention, and the error introduced by the hydrolysis of dextrin is less even when the most favorable method of inversion is used; *viz.*, heating for ten minutes, regulating the temperature so as to reach 68° at the expiration of that time.

OHIO STATE UNIVERSITY,  
COLUMBUS, OHIO.

---

## METHOD OF DETERMINING CHROMIUM IN CHROME ORE.

BY EDMUND CLARK.

Received February 8, 1895.

PROF. STORER and others have suggested the use of nitric acid and potassium chlorate as agents for the oxidation of chromic compounds to chromic acid. Using this suggestion as a basis for the determination of chromium in chrome iron ore, I have experimented with a method which has proved both practicable and accurate.

For complete analysis a half gram sample of the finely ground ore is weighed into a platinum crucible with a capacity of not less than fifty cc. The ore is covered with twenty-five grams of potassium bisulphate and fusion is commenced over a Bunsen burner with very low flame which is protected from air currents by a sheet iron chimney.

To insure complete fusion, and to guard against any loss, the operator must manipulate carefully and watch the operation from beginning to end. At first, the flame should be so low as to fuse the bisulphate very slowly.

After the mass is in a liquid condition, and there is no longer any danger of loss from spattering, the crucible is grasped with a pair of crucible tongs and the contents are run up around the sides, in order to seize hold of any particles of ore which may have become stranded there.

At this stage of the process, the flame may be increased a little so as to cause a tolerable redness of the bottom of the crucible.

At intervals of ten minutes the crucible must be manipulated by the operator as before described. Forty minutes will suffice for complete decomposition of the ore. Pour the contents into a perfectly clean and dry, four to five-inch platinum evaporating

dish, making as thin a layer of the mass as possible. Place the crucible and cover in a twelve-ounce beaker and reserve for the solution.

Cool the contents of the dish quickly by means of a shallow vessel of cold water, which should be immediately at hand. Cover the dish with a suitable watch-glass to prevent loss of particles by the sudden contraction of the cooling mass. When cool, rinse off the watch-glass and add thirty-five cc. of hydrochloric acid (1.20 sp. gr.) and twenty-five cc. of water.

Boil quietly over the flame, keeping the watch-glass on, until the solution is complete, usually requiring about fifteen minutes. Transfer the solution, with care, to the beaker containing the crucible and warm on the steam-bath until the crucible and cover can be washed free from the bisulphate fusion. The solution now occupies about 100 cc.

Let contents practically settle, then decant the clear supernatant fluid into another twelve-ounce beaker and add fifteen cc. more of hydrochloric acid to the residue. Heat on the steam-bath until nothing but silica remains undissolved. Unite solutions and filter, reserving the filtrate and igniting the filter. Weigh as silica.

The filtrate, which should be easily contained in a twelve-ounce beaker, is now rendered slightly alkaline with ammonia.

The dirty, reddish green precipitate consists of the hydroxides of chromium aluminum, and iron. These are warmed on the steam-bath until the smell of ammonia is faintly perceptible. Filter on a fifteen cm. filter without washing and dissolve the collected hydroxides into the original beaker, with dilute hydrochloric acid. Reprecipitate with ammonia and collect on the same filter as before, washing carefully three times with hot water, combine the two filtrates, and in the united solution determine lime and magnesia by any good method.

Transfer the filter containing the precipitated hydroxides to a four and one-half inch porcelain evaporating dish and cover with a five-inch watch-glass. Add fifty cc. of nitric acid (1.42 sp. gr.) and heat gently over a Bunsen flame. From time to time carefully add potassium chlorate with a small glass or porcelain spatula. The addition of this reagent is attended with small

explosions, which should be reduced in violence, as much as possible, by adding small quantities and not too frequently. Great care should be taken here to avoid loss from spattering.

The gradual oxidation may be noticed by the changing of the dirty green color of the emulsion to a clear orange-red solution. The organic matter of the filter-paper has been completely oxidized along with the chromic hydroxide. The complete oxidation is easily detected, but a small excess of potassium chlorate is added to insure it. The chromium now exists as chromic acid.

Transfer the solution to a twelve-ounce beaker, making up to about 150 cc. with water, and precipitate the iron and alumina with ammonia. Filter into a sixteen-ounce beaker without washing. Dissolve the precipitate on the filter with warm, dilute nitric acid and wash thoroughly, allowing the solution to run into the beaker in which the precipitation was made. Reprecipitate with ammonia and throw the precipitate on the same filter, allowing the filtrate to be caught in the same beaker as was the first filtrate. Separate, and determine, the iron and alumina by any good method.

The ammoniacal filtrate contains the chromium as ammonium chromate. Acidify with hydrochloric acid and add a sufficient quantity of strong sulphurous acid water to completely reduce the chromium. The clear, bright green color imparted to the solution is an indication of the complete reduction.

The excess of sulphurous acid must be driven off. This may be done by boiling, but it may be accomplished in a highly satisfactory manner by leaving the open beaker remain on a steam-bath over night.

Upon the complete removal of the sulphurous acid, the solution is rendered just alkaline with ammonia, with a final addition of three or four drops in excess. Stir well with a glass rod and heat over a lamp until the smell of ammonia is only faintly perceptible. We have, now, a precipitate of chromium hydroxide ready for filtration. Filter on a 12.5 cm., filter and allow it to drain without washing out the beaker or washing the precipitate. After the precipitate has drained, wash it carefully back into the beaker by inverting the funnel and using warm water. Add more warm water and stir to insure complete solution of all alkaline salts.

Throw the precipitate back upon the same filter and wash three times with hot water. Drain, dry, and ignite in a platinum crucible and weigh as chromium sesquioxide.

Another method of determining the chromium in the yellow solution of ammonium chromate, and one which many chemists may consider the more expedient, is as follows :

Moderately acidify the ammonium chromate solution with acetic acid and warm. Add an excess of a clear solution of plumbic acetate and allow the precipitate of plumbic chromate to settle in a warm place for several hours ; then collect on a weighed filter (previously dried at  $100^{\circ}$  C.) and wash with cold water.

Dry at a temperature of  $100^{\circ}$  to  $110^{\circ}$  C. and weigh. The increase of weight is the weight of the plumbic chromate, from which the percentage of chromic oxide may be calculated.

The choice given to either of these methods for the final precipitation of chromium is purely arbitrary.

In a future article the method employed in the estimation of chromium in chrome steel and ferro chrome will be dealt with.

---

### NEW BOOKS.

PROCEEDINGS OF THE ELEVENTH ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, BULLETIN No. 43, U. S. DEPARTMENT OF AGRICULTURE, DIVISION OF CHEMISTRY, EDITED BY DR. H. W. WILEY. pp. 403. Washington : Government Printing Office. 1894.

This bulletin issued annually through the courtesy of the U. S. Department of Agriculture, contains, as usual, the results obtained by the various reporters appointed by the Association, a general discussion of their reports, and a complete summary of the methods of agricultural chemical analysis which are now almost universally used in this country and which have official recognition.

Some sixty chemists participated in the meeting, and the very full discussions denote a lively interest in the work. For the first time a committee was appointed to consider the changes of method recommended by the various reporters and to approve the same before submitting them for action. Most of the changes recommended were approved by the committee. It is, however, gratifying to note that these changes were, as a rule, unimpor-

tant. The analyses made for nitrogen by the official methods agree closely and the only change made was in the wording of the Gunning method modified to include nitrates. The Tiemann-Schulze method for nitrates alone, was adopted as a provisional method until a better could be found although the reporter was instructed to continue his efforts in this direction. The use of two and five-tenths per cent. acid and alkali was dropped from the method of crude fiber determination leaving the one and one-fourth per cent. solution alone official. The dilute ammonia for washing magnesium pyrophosphate was made more definite in strength by prescribing a two and five-tenths solution, and Pemberton's volumetric method for estimating phosphoric acid appears quite promising and bids fair, after further study, to become official. No co-operative work was done on dairy products either from satisfaction with our present methods or from lack of interest. One or two changes in the methods for potash were made for the sake of uniformity. The report on soil and ash analysis was quite full and an unusually large number of chemists took part in the investigation. This is the more surprising as the analyses are very tedious and a large outlay of time was necessary. The results too are unsatisfactory both on ash and on the soil solutions, in view of which the question may well be raised as to how our general methods of mineral analysis would compare in the hands of different analysts. The changes of method adopted for soil analysis have already been printed in this JOURNAL, 16, 792. One noteworthy point brought out by the reporter as a result of his work and that of other chemists is that the best glass is fully as good as the best porcelain for the solution of silicates and that no appreciable error will be introduced by its use. A reporter on tannin was appointed for next year and provisional methods adopted. The reporter on fermented liquors was also instructed to include the analysis of distilled liquors in his next year's investigations. Nearly 150 pages of the bulletin are covered with abstracts of agricultural chemical articles and represent the year's work of the abstract committee.

There seems to be a growing conservative feeling among the members in regard to alterations of method as a result of some

past mistakes. This is to be commended but should not be carried so far as to become prohibitive. The best results will be reached when good judgment and conservatism go hand in hand. Many will doubt the wisdom of the change made in the constitution itself, prohibiting any change, except by unanimous consent, in the methods of fertilizer analysis until an opportunity shall have been given all official chemists to try the same. This gives to any one member a power to delay action which many will think should be held by the majority alone. The appointment of reporters for two years, and associates who shall fit themselves to become reporters on the special lines of work, should meet the approval of all chemists and may be far-reaching in its results. The Secretary of the Association has not felt himself impowered to make any alterations whatever in the wording of the methods; and it is pleasing to learn that a special committee has been appointed to rewrite the methods and put them in creditable English.

There is a growing feeling in the Association that it is reaching the point where it can well enlarge its scope. In the past it has confined itself strictly to analytical processes, but the desire seems to be increasing for investigations along the line of availability in fertilizer and food material and to make more of a study of proximate constituents. General dissatisfaction is expressed with the present "citrate-soluble phosphoric acid," "crude fiber," "nitrogen-free extract," etc., and it is to be hoped that dissatisfaction will lead to renewed investigations. The Association has an additional and unlimited field of usefulness for itself along this line.

C. L. PARSONS.

BIBLIOGRAPHY OF ACETO-ACETIC ESTER AND ITS DERIVATIVES. BY PAUL H. SKYMOUR, M.S., INSTRUCTOR IN CHEMISTRY, LAKE FOREST UNIV. Smithsonian Miscellaneous Collections, No. 910. pp. 147. Washington: Smithsonian Institution. 1894. Price 75 cents.

The rapidly increasing literature of aceto-acetic ester makes this volume of great value. The author has given brief abstracts of the articles that have appeared upon the subject of the bibliography from 1840-1891, "omitting what had no relation to aceto-acetic ester." The abstracts are clear, and full enough to

accomplish their time-saving purpose. Misprints are infrequent. On page 107, however, we find "uvitic acid" and "carbuvitic acid" instead of uvic acid and carbuvic acid. Excellent author and subject-indexes accompany the abstracts.

L. B. H.

REPORT ON THE EXTENT AND CHARACTER OF FOOD AND DRUG ADULTERATION, BULLETIN No. 41, U. S. DEPARTMENT OF AGRICULTURE, DIVISION OF CHEMISTRY. BY ALEX. J. WEDDERBURN. pp 64. Washington: Government Printing Office. 1894.

EIGHTH ANNUAL REPORT OF THE DAIRY AND FOOD COMMISSIONER OF OHIO. BY F. B. MCNEAL, COLUMBUS, OHIO.

FIRST ANNUAL REPORT OF THE COMMISSIONER OF AGRICULTURE OF NEW YORK. BY F. C. SCHRAUB, ALBANY, N. Y.

A COMPILATION OF THE PHARMACY AND DRUG LAWS OF THE SEVERAL STATES AND TERRITORIES, BULLETIN No. 42, U. S. DEPARTMENT OF AGRICULTURE, DIVISION OF CHEMISTRY. BY ALEX. J. WEDDERBURN. pp 152. Published by order of Congress. 1894.

There seems to be a growing interest among our legislators and among the general public in reference to pure foods and drugs. Many of the states and, in fact, a majority have laws making druggists responsible for the drugs they sell, requiring that only pure dairy products shall be sold, and placing a standard on commercial vinegar, but in most instances the laws have simply served to adorn the statute books. Much work has been done to arouse the public, and in view of the strict control exercised on adulteration in most other advanced countries, it is surprising that it has not met with more immediate success. The cause has undoubtedly been injured by grossly exaggerated articles claiming general impurity of all our food products, but enough adulteration, proved by actual analysis by competent chemists, is now coming to light to demand immediate enlargement and enforcement of our laws.

The chief records of recent opinions and analyses will be found in the above reports. Among the replies received by the special agent of the Department of Agriculture and recorded in Bulletin No. 41, will be found many statements by some of our best chemists. These are, in general, noteworthy for their conservative tone but, as a rule, each has had some form of adulteration come under his personal notice, and those whose duties have caused them to investigate the matter, give many examples of foods,

drugs, and dairy products, which they have found badly falsified.

It seems to have been left, however, for the Food and Dairy Commissioner of Ohio to make the first really important move in this matter, and the results tabulated in his Eighth Annual Report make extremely interesting data for chemists at large. It is true that in Massachusetts, New York, Wisconsin, and a few other states, a good many cases have been prosecuted for violation of the laws, but the examination of food products have been made mainly to prevent the watering and skimming of milk and the substitution of oleomargarine for butter. In Ohio, however, there is a much broader clause in the law, to the effect that "any article made of or sold under the name of another article, or falsely branded, or upon which art has been used to conceal inferiority, or in which there is fraud or deceit," shall be deemed illegal. Upon this basis the efficient Commissioner, Mr. F. B. McNeal, appears to have attempted, without fear or favor, to purify the food stuffs of all kinds sold within his jurisdiction. His work has been eminently successful, the results are widely quoted, and several states are apparently about to appoint Commissioners to follow his example. Among the substances found adulterated, baking-powder, buckwheat flour, butter, cider, coffee, chocolate, condensed milk, fruit-butter, honey, jelly, oleomargarine, olive-oil, preserves, quinin pills, vinegar, and wine, were impure in at least half of the samples analyzed, and in some cases there was not a particle of the substance itself present. Other noteworthy examples of impurity were in pepper, milk, mustard, cream of tartar, etc., and it will be specially interesting to note that butter added to oleomargarine is considered also in the light of an adulteration. The analyses are printed in more or less detail and will be useful to any chemist for reference. All, however, will deplore the fact that no methods, or references to methods used, are given, and also that the word "about" is not more frequently printed to modify the results. The statement of exact percentages of butter-fat in oleomargarine, of the various impurities in coffee, of foreign fats in butter, of the water added to milk, etc., are impossible, and when so directly made are misleading to the general public and cause much trouble for conservative chemists when they are quoted against them in the



courts. With this exception there is little to criticise in the report, and it is certainly to be hoped that many others showing equal results will follow.

The First Annual Report of the Commissioner of Agriculture of New York is practically a continuation of the reports of the previous dairy commissioner. The report contains many analyses, but they are confined almost wholly to dairy products, oleomargarine, and vinegar. In the sub-report of the cheese instructor, will be found a full and detailed account of the investigations on cheese planned by Mr. Van Slyke, the chemical features of which have already been published by him in this JOURNAL, 15, 605, 635, 645, and 16, 712, and the Bulletins of the New York Experiment Station. One important feature of the report is the summary of the laws of all the states on foods and dairy products. From this summary it appears that the requisite standard for milk varies between twelve per cent. and thirteen per cent. solids, eighty-eight per cent. and eighty-seven per cent. water, and three per cent. to three and one-half per cent. fat, and condensed milk must be made by the evaporation of standard milk without addition of other matter. The standard for vinegar varies between a minimum of four per cent. to four and one-half per cent. acetic acid and cider vinegar must have at least two per cent. cider vinegar solids. Vinegar cannot contain any sulphuric acid, lead, copper, or other deleterious substance. In regard to oleomargarine, Massachusetts and Ohio forbid its sale if colored in imitation of yellow butter. In New Hampshire, Vermont, West Virginia, and Minnesota, it must be colored a bright pink. Pennsylvania, Virginia, Missouri, and Delaware, prohibit its sale altogether. There seems to be no detailed laws in regard to other food products.

The bulletin of the Department of Agriculture on Pharmacy and Drug Laws will serve mainly as a place of reference for legal information. Most of the states now require all persons compounding or dispensing drugs to pass rigid examinations and receive certificates of registration. Poisons are restricted in sale and must generally be labeled in red letters, and sales entered in a special poison registry book. Many of the states make the druggist responsible for the purity of the drugs he sells, while

others make him responsible only when he is aware of their character.

Altogether the four reports show a growing interest in the subject of adulteration and an increasing tendency to legislate on the subject. It would appear, however, that no general results will be obtained until there is some national law which will regulate the trade between states in adulterated goods. When such a law is passed we may soon expect an efficient control and a consequent greater field for chemical usefulness and employment.

C. L. PARSONS.

KRÄFTE DER CHEMISCHEN DYNAMIK. VON DR. LUDWIG STETTENHEIMER. pp. 88. 8 vo. Frankfurt am Main: H. Bechhold. 1895. Price, 6 m.

These three lectures appear to have been held before a mixed audience, containing probably more mathematicians or physicists than chemists. They are of a polemical nature, against the molecular hypothesis, but they confine themselves to general problems and do not touch at all upon the purely chemical relations, such as those of isomerism, polymerism, and organic reactions. As far as can be extracted from a somewhat involved line of argument every substance whether a mixture, compound, or simple substance is to be regarded as a homogeneous individual as long as chemical reaction does not take place. There is no separation into molecules, but every atom reacts upon every other atom in a purely mechanical way, as do the celestial bodies; atoms near one another simply influencing each other to a larger degree than those further apart. The introduction of any new atoms, whether of the same or of another sort, disturbs the equilibrium which can be restored either by an equal distribution of the new atoms throughout the mass without disturbing the relative positions of the old atoms, or by a total rearrangement of the positions.

In the discussion of the solid state, views similar to those of the late T. Sterry Hunt are developed, but they are extended over the liquid and gaseous condition as well.

All disturbances of the relative positions of the atoms are considered chemical reactions, whether these be performed by simply separating them mechanically, as in pouring half of a liquid into another vessel, or by what are ordinarily known as chemical changes or, by electrolysis, change of aggregation, etc. The

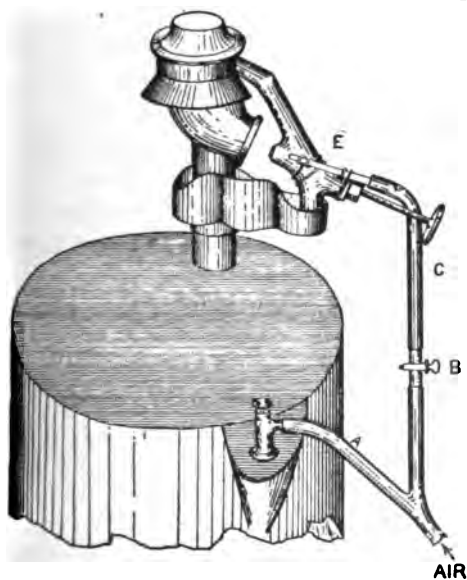
various modes of energy are all considered to depend exclusively upon relative changes of position between the atoms. Such views as those of Williamson's hypothesis are discarded because atoms are not even momentarily associated into real molecules.

It is difficult to criticise the reasoning, inasmuch as it is based upon the most general forms of phenomena and deals with these in the largest possible fashion, dealing with infinitesimal disturbances in very large masses. Until the subject is applied to purely chemical reactions in greater detail no gain can be perceived in these new assumptions. The grounds upon which the molecule, as a physical identity, is abandoned, appear to be somewhat trivial.

M. L.

## NOTES.

*An Improvement on the "Dangler's Laboratory Lamp."*—The enclosed sketch illustrates an improvement on the "Dangler's Laboratory Lamp."



B. Glass stop-cock.

C. Rubber tubing.

E. Glass tip kept in place by a copper wire.

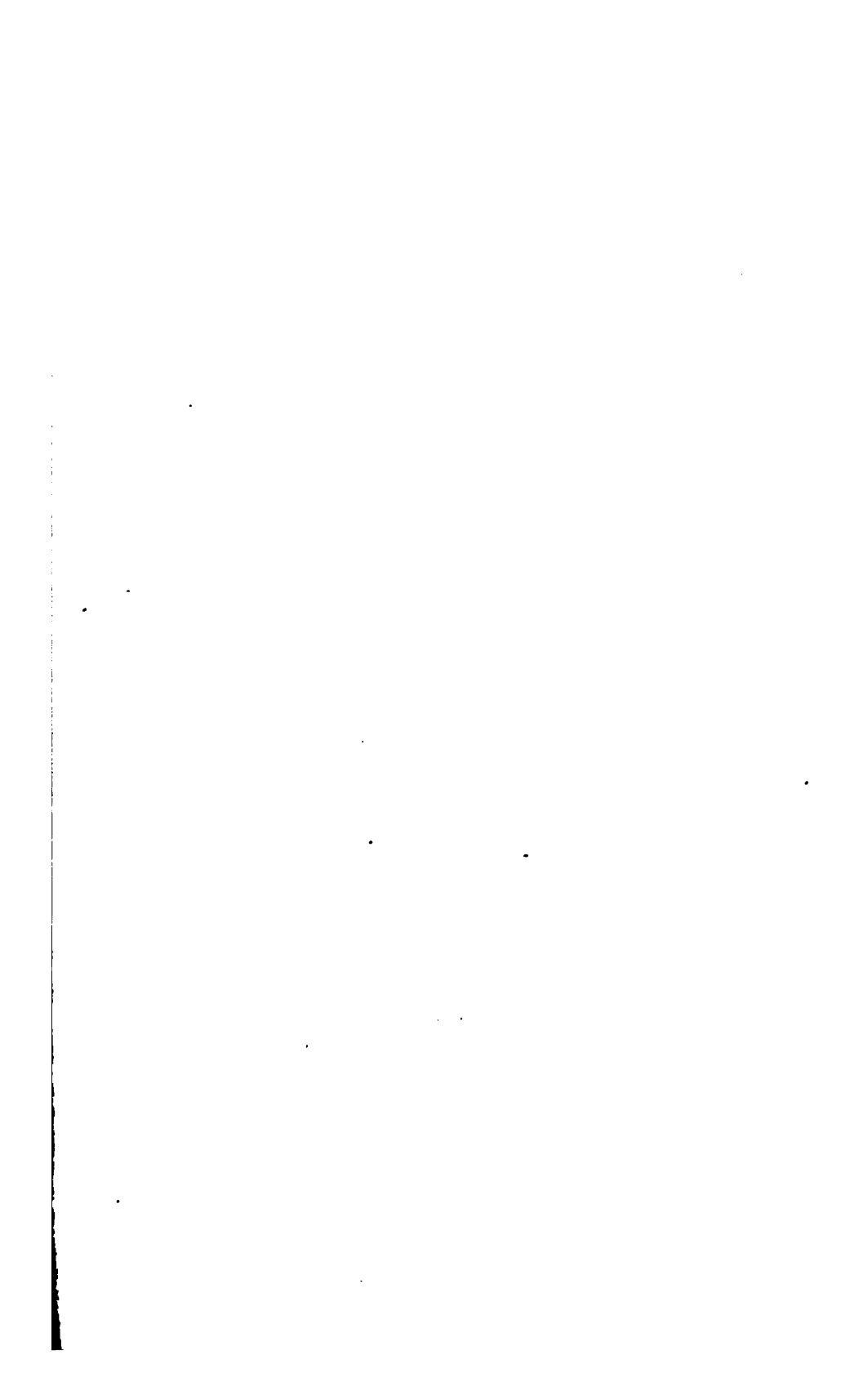
After using this lamp for about two years it began to burn with a smoky flame. I then introduced a small jet of air into the flame as shown. By the help of the glass stop-cock the air is regulated, while a steady pressure is exerted on the gas-line through the side tube A. In this way the lamp will burn all day with a uniform and most perfect flame, strong or weak, as desired; no gas-burner can possibly give better satisfaction.

The air-blast is obtained from a Bunsen filter-pump, which is supplied with water from an artesian well.

ANDREW LUNDTRIGEN.

*Spurting in Cupellation.*—Dr. H. G. Torrey, of the N. Y. Assay Office, writes to the *Engineering and Mining Journal*, under date of February 26, that a comparative test of old and new cupels has been made with reference to their liability to spurt and thereby cause loss in the muffle. The test was made on 1,000 each of cupels less than one week old and about one year old. "In each case the number of cupels that spurted was the same, being only about one per cent. \* \* \* The result of all the different experiments [which we have made] is that the spurting is due not to moisture, but to the escape of gas arising from the decomposition of impurities remaining in the cupel, and that this gas not only takes time but a high heat to expel."

*A Substitute for Hydrogen Sulphide* is found by Schiff and Tarugi in thioacetic acid made by acting on glacial acetic acid with phosphorus pentasulphide. The solution, for students' use, is made by dissolving the acid in a slight excess of dilute ammonia, and is given out in bottles having a pipette holding about two cc. thrust through the cork. About one-half to one gram of substance, dissolved in hydrochloric acid, is treated, while hot, with one and one-half to two cc. of a thirty per cent. solution of the above ammonium thioacetate. The sulphides are completely separated; even arsenates are completely decomposed. *Ber. d. chem. Ges.*, 27, 3437.





*H. B. Nason*

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

---

### HENRY BRADFORD NASON.

Henry Bradford Nason, Professor of Chemistry and Natural Science at the Rensselaer Polytechnic Institute, Troy, N. Y., died of apoplexy, at his home, on January 17, 1895.

Professor Nason was a former president of the American Chemical Society, and for very many years an active, interested, and energetic member.

During the early days of the Society, long before it had acquired its present established footing, he stood as one of its staunch supporters, and never despaired of its eventual and permanent success; a faith which to-day has become reality.

Those who were so fortunate as to know Professor Nason personally, will remember with pleasure that scientific attainments were associated in him with a cheerful and kindly nature, eminently qualified to win many and lasting friends.

He was the son of Elias and Susanna (Keith) Nason, and was born at Foxborough, Norfolk County, Mass., June 22, 1831. In November, 1841, he moved to North Bridgewater, Mass., the native place of his mother, who died the year previous. In 1843 he attended a school for boys kept by Mr. Savory at Newburyport, Mass. From 1844 to 1847 he attended the Adelphian Academy at North Bridgewater, now Brockton, Mass. In December, 1847, he entered Williston Seminary, Easthampton, Mass., graduating in 1851. He entered Amherst College and graduated in 1855. September 1, 1855, he sailed from New York to London on the ship Amazon, having a passage of thirty-five days. He travelled through Holland, Belgium, up the Rhine to Frankfort

and then to Göttingen, where he was matriculated as a student of philosophy October 24, 1855. While connected with the university he devoted his time to chemistry, mineralogy, and geology, and attended lectures on physics and botany, graduating in the Summer of 1857. He spent a short time at Heidelberg and Freiburg and then visited Berlin, Paris, and London. He spent the Winter of 1857-58 in teaching at the Raymond Collegiate Institute, Carmel, Putnam County, N. Y. In April, 1858, he was appointed professor of natural history in the Rensselaer Polytechnic Institute. In the Summer he declined an appointment as professor of chemistry and natural science in Oahu College, Hawaiian Islands. He accepted an appointment to the same chair in Beloit College, Wisconsin, in September, 1858, and spent a part of each year there, the remainder of the time at Troy, until 1866, when he resigned the position at Beloit to accept the professorship of chemistry and natural science at the institute, which position he held until his death.

From 1855 to 1857, while connected with the university at Göttingen, during vacations he made the tour of Europe. In the Spring of 1860 he travelled through the southern portion of the United States. He sailed for Europe in July, 1861, and travelled through Great Britain, and afterward went to Italy, Sicily, and southern France, spending considerable time in the study of volcanic phenomena. He spent the Summer of 1872 in California, Nevada, and Idaho. In the Autumn he made a second visit to California, visiting the mining regions of Colorado and Utah. In 1875 he made a third trip to California, visiting the Yosemite, northern California and Nevada. He spent the Summer of 1877 in visiting northern Europe, Finland, and Russia.

In 1877 Professor Nason was appointed by President Hayes juror for the United States Government at the Paris Exposition and was assigned the department of mineralogy and metallurgy.

In 1884 he visited northern Europe and the fiords and glaciers of Norway, extending his travels to the North Cape.

Professor Nason published "Inaugural Dissertation on the Formation of Ether," 1857; "Table of Reactions for Qualitative Analysis," 1865; translated and revised "Wohler's Handbook



of Mineral Analysis," 1868; "Table for Qualitative Analysis in Colors," 1870; edited Elderhorst's "Manual of Blowpipe Analysis," 1873; fourth and fifth editions of the same, 1875-76; edited "Manual of Blowpipe Analysis and Determinative Mineralogy," 1880; compiled "Semi-Centennial Catalogue of the Rensselaer Polytechnic Institute," 1874, and edited "Proceedings of the Semi-Annual Celebration" of the same institution, 1874; edited "Biographical Record of the Officers and Graduates of the Rensselaer Polytechnic Institute," 1886.

In 1857 he received the degree of A.M. and Ph.D. from the Georgia Augusta University, Göttingen; in 1864 the honorary degree of A.M. from Amherst College; in 1880 the honorary degree of M.D. from the Union University of New York, and the same year the honorary degree of LL.D. from Beloit College, Wisconsin. He has been elected fellow of the American Association for the Advancement of Science, fellow of the London Chemical Society, fellow of the Society of Chemical Industry, England, member of the American Chemical Society, corresponding member of the New York Academy of Science, member of the American Institute of Mining Engineers, member of the Troy Scientific Association, honorary member of the Albany Institute, member of the Norske Turistforenings, Christiana, Norway; elected member of the University Club, 1883, and of the Union League Club, New York City, 1886.

W. P. MASON.

## METHODS FOR THE DETERMINATION OF MANGANESE.<sup>1</sup>

By W. S. THOMAS.

Received February 11, 1895.

**F**OR some time no satisfactory method for the rapid determination of manganese has been in use in this laboratory; all proposed schemes have been, from time to time, successively tried and none have withstood the tests under all conditions.

With the great demand now made for chemical analyses by which metallurgical and manufacturing processes are controlled, it has been no small part of the chemist's work to devise rapid methods for making these determinations, so necessary for the information of the metallurgist and manufacturer.

<sup>1</sup>This and the paper following it are reprinted from the Bulletin of the Missouri Mining Club, published at the Missouri School of Mines, Rolla, Mo.

In order to supply this need, every rapid method now in use and generally known or published, has been introduced into the course of instruction known as Technical Analysis in this laboratory.

During the past two years the determination of manganese has been attempted by using a method published in the *Journal of Analytical and Applied Chemistry* by A. H. Low, but so far as the method has been applied in this laboratory it has proven of no value, owing to the low results obtained.

For the purpose of arriving at a satisfactory conclusion in regard to the Low method, a series of experiments were begun, using manganese carbonate, and manganese sulphate, from which most of the water of crystallization was driven off and the sample kept in a corked tube. In order to check the volumetric work the metallic content of both salts was carefully determined by gravimetric analyses, in which the manganese was precipitated as manganese ammonium phosphate, ignited, and weighed as pyrophosphate.

This method gave very closely agreeing results by duplicate analyses of the respective salts, the filtrate in each case being tested for manganese by means of ammonium sulphide and only mere traces of manganese found.

A standard solution of potassium permanganate was made in which 6.312 grams of potassium permanganate were dissolved in two liters of distilled water, and a solution of 11.46 grams of  $C_2H_2O_4 + 2H_2O$ , (oxalic acid), in one liter of distilled water, kept well corked and away from the light.

In obtaining an experimental standard, ten cc. of the oxalic acid solution were taken and five cc. of sulphuric acid added, and the whole titrated with standard potassium permanganate, one cc. = 0.0056 gram of iron, the strength of the oxalic acid being calculated from the data obtained.

It was found that ten cc. of oxalic acid reduced 20.1 cc. of the standard potassium permanganate, one cc. of which equals 0.0011 gram manganese, based on the equation  $10FeSO_4 = K_2Mn_2O_8$ . Therefore one cc. oxalic acid equals 0.002211 gram manganese.

By calculation based upon the equation (Low's)



126 parts of oxalic acid equal fifty-five parts of manganese. Knowing the weight of oxalic acid in one cc. of solution and introducing this into the proportion, one cc. of oxalic acid solution was found to be equivalent to 0.005 gram manganese.

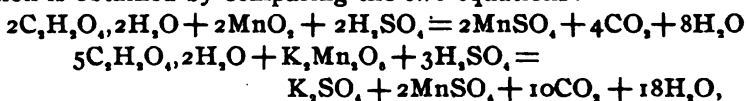
From these two methods we obtain two entirely different strengths, neither of which give satisfactory results, as will be seen by calculations based upon titrations, made according to Low's instructions.

A half gram of manganese sulphate, which gave 34.64 per cent. manganese by gravimetric analysis, was taken and made up to 500 cc.; fifty cc. were taken for each titration, zinc oxide was added in the usual way, and bromine water to precipitate the manganese as manganese dioxide, the excess of bromine boiled off, solution filtered, the precipitate well washed with hot water, and the filter with its contents replaced in the flask where the precipitation was made; fifty cc. of dilute sulphuric acid added and a measured volume of oxalic acid run in from a burette; the excess of oxalic acid determined by treating with the standard potassium permanganate. Nine titrations by Low's method gave the following results:

No.	$C_2H_2O_4 \cdot 2H_2O$ added.	Excess of $K_2Mn_2O_8$ .
1	10 cc.	13.6 cc.
2	10 "	13.6 "
3	10 "	13.4 "
4	10 "	13.6 "
5	10 "	13.8 "
6	10 "	13.5 "
7	10 "	13.8 "
8	10 "	13.8 "
9	10 "	14. "

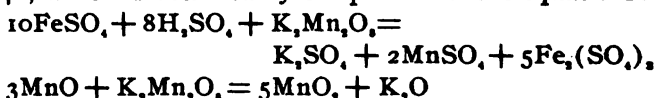
Taking a mean of the excess as 13.6 cc. of potassium permanganate, and multiplying by 0.0011 (one factor of the strength of the permanganate) and dividing by 0.002219 the strength of one cc. of oxalic acid in terms of potassium permanganate, we obtain the amount of oxalic acid oxidized by the 13.6 cc. of potassium permanganate, which, subtracted from ten cc. gives the number of cubic centimeters of oxalic acid oxidized by the manganese dioxide derived from the sample. Multiplying this by 0.0055 + and correcting for one gram, we obtain 35.64, which is

one per cent. above the gravimetric result as the per cent. of manganese in the sample. The factor  $2\frac{1}{2}$  used in this calculation is obtained by comparing the two equations:



from which is readily seen, that the strength of one cc. of oxalic acid in terms of potassium permanganate is  $2\frac{1}{2}$  of its strength in terms of manganese dioxide, from which we can derive a strength for oxalic acid based on experiment and not on calculation, as set forth in another place.

Titrating the same sample of manganese sulphate by Volhard's method, in which the strength of the potassium permanganate in terms of iron equal to 0.0056 gram, is multiplied by the factor 0.2946, which is obtained by comparison of the equations:



(in which  $\text{K}_2\text{Mn}_2\text{O}_8 = 10\text{FeO}$  and  $3\text{MnO}$  respectively) the following results were obtained: One-half gram of substance taken and made up to 500 cc. and fifty cc. taken for each titration.

No. of titration.		Cubic centimeters of $\text{K}_2\text{Mn}_2\text{O}_8$ used.
1	50 cc. solution.	10.3
2	50 cc. solution.	10.3
3	50 cc. solution.	10.3

Multiplying this result by 0.2946 and correcting for one gram we get thirty-four per cent. manganese or 0.64 per cent. less than by the gravimetric analyses.

The methods were both tried upon a sample of manganese carbonate, which gave, by means of manganese pyrophosphate, forty-five per cent. of manganese. Several samples of one-half gram were taken and a few titrations made from each with the following results. Six titrations by Low's method gave

No.	$\text{C}_2\text{H}_2\text{O}_4, 2\text{H}_2\text{O}$ added.	Excess of $\text{K}_2\text{Mn}_2\text{O}_8$ .
1	10 cc.	12.9 cc.
2	10 "	12.6 "
3	10 "	13.0 "
4	10 "	12.3 "
5	10 "	12.3 "
6	10 "	12.9 "

Throwing out No. 3, the average volume of potassium permanganate reduced by the excess of oxalic acid equals 12.6 cc. and applying the same calculations as before, we obtain 41.03 per cent., or four per cent. less than by gravimetric analyses.

Eight titrations by Volhard's method gave the following results:

No.	Solution.	K <sub>2</sub> Mn <sub>2</sub> O <sub>8</sub> added.
1	50 cc.	13.5 cc.
2	50 "	13.5 "
3	50 "	13.5 "
4	50 "	13.4 "
5	50 "	13.5 "
6	50 "	13.4 "
7	50 "	13.5 "
8	50 "	13.5 "

When corrected for one gram these titrations give 44.54 per cent. manganese, or 0.46 per cent. less than the gravimetric analyses.

The results obtained with Low's method are in one case approximate, but, when the same manipulations are applied to as much as one-half gram of substance, the result is nearly fifty per cent. too low. Theoretically the method is perfect, but I have been unable to obtain the theoretical results in practice, and in so far as this is the important feature, the method has proved worthless in my work.

Volhard's process is very rapid and simple in its application. The manganese should be in the form of a proto salt, which is the form obtained by the procedure in decomposing an ore. Iron is removed by means of zinc emulsion,  $3\text{ZnO} + \text{Fe}_2\text{Cl}_6 = \text{Fe}_3\text{O}_4 + 3\text{ZnCl}_2$ , which converts the iron into insoluble ferric oxide by vigorous shaking.

This having been done, the solution, precipitate and all, is made up to 500 cc.; fifty cc. is taken out by means of a pipette, placed in a twelve-ounce flask, 250 to 300 cc. of hot water added, heated to boiling, standard potassium permanganate run in, and the solution shaken after each addition of potassium permanganate. A bulky brown precipitate of manganese dioxide is formed and the pink color of the solution is destroyed until the manganese is all oxidized to manganese dioxide, when a drop of

the permanganate imparts a pink color to the solution. A few trials will enable the operator to ascertain this point with accuracy and rapidity.

This work was conducted more for the purpose of ascertaining the values of the methods when working with the rapidity which is required in actual practice, than for absolute accuracy, to 0.01 or 0.001 per cent. I have no doubt that Volhard's process can be made to check closer than 0.64 or 0.46 per cent. respectively, of the metallic content of an ore, but in practical metallurgical analyses, it is not always practicable to exercise the necessary precautions. The method is capable of wide application, and where rapidity is essential, is sufficiently accurate in most, if not all cases.

### THE WET ASSAY FOR COPPER.

By R. S. DULIN.

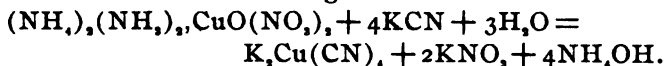
Received February 11, 1895.

IT seems difficult for the metallurgical chemists of this country to settle upon a uniform method for the rapid determination of copper. We should have a standard method, applicable for all commercial work, which would be fairly accurate under as many possible varying conditions, so that results obtained from the same ore, by different chemists, should be substantially uniform. For about nine months past I have been engaged upon an extended series of experiments, having for their object a determination of the chief causes for variation and error in the methods most generally employed and for the purpose of finding a modification of common methods which would be an improvement upon those now used. At the same time I have made myself conversant with much of the current literature upon the subject and the observations herein offered, while based upon my individual experiments, are corroborated, in most part, by the published results of others.

There are at present three well-recognized methods employed in the United States for the determination of copper. Each method has its own advocates, and it is perfectly fair to say, that either method in the hands of a skilled chemist, thoroughly understanding the reactions of the methods, working with all due care, will yield substantially the same results. The methods referred to are :

1. The cyanide method. 2. The iodide. 3. The electrolytic. A colorimetric method is also employed for the determination of copper, when the percentages fall below two per cent. I have made no particular study of this method, and as it is only employed in special cases, I shall make no further reference to it.

The cyanide method depends upon the fact, that when a solution of potassium cyanide is run into an ammoniacal solution of copper the blue color is discharged. The reaction is as follows :



This method is fully described in Furman's Manual of Practical Assaying. The following precautions should always be carefully observed. 1. The bulk of the liquid titrated should always be uniform. By inattention to this an error of from two to three per cent. is possible. 2. The solution should always be cooled to the temperature of the laboratory before titrating, otherwise an error of about three per cent. is possible. 3. The amount of ammonia added should be nearly constant, otherwise the possible error may amount to as much as five per cent., or even more.

These precautions are general and must always be carefully observed, in every modification which may be made in the method. In the ordinary modification of the method, ferric hydroxide is almost certain to be precipitated, upon the addition of the ammonium hydroxide. If the amount be small, no error is apt to occur, but it should always be filtered off. If the amount be large, it is not easy to wash out all of the copper salt, thereby causing lower results, unless large quantities of wash-water are employed, thus increasing and varying the bulk. The error arising from increased bulk may be obviated, by taking, after mixing; an aliquot part of the solution; if the solution be not thereby made very dilute, the error is so slight that it may be neglected. If salts of manganese are present, the end reaction cannot be determined, owing to the liquid first turning green, finally black. The presence of large quantities of calcium, I found, confused the end reaction, causing error of importance. Experiments made showed that magnesia did not interfere, and the presence of antimony and arsenic was found to cause no sensible variations.

Zinc, which is almost certain to be present in varying amount, is a possible source of great error. The following results were obtained from a large number of carefully conducted experiments. Only the averages are given and they are substantially the same as the extremes. In these experiments the bulk of the liquid varied from twenty-five to as much as fifty cc., thereby causing a slight error, for which no correction has been made. This error would not substantially change the results. Careful attention was paid to the precautions previously enumerated.

Weight of copper.	Weight of zinc.	Cyanide used.	Increase.
0.05	0.00	10.4 cc.	
0.05	0.01	11.0 "	0.6 cc.
0.05	0.02	11.7 "	1.3 "
0.05	0.03	12.3 "	1.9 "
0.05	0.04	12.9 "	2.5 "
0.05	0.05	14.0 "	3.6 "
0.05	0.06	16.1 "	5.7 "
0.05	0.07	18.9 "	8.5 "
0.05	0.08	21.6 "	11.2 "
0.05	0.09	24.3 "	13.9 "

These results show that there is a gradual increase of about six-tenths cc. in the amount of the cyanide solution required, until the amount of zinc present nearly equals the amount of copper, when the increase becomes variable, until the amount of zinc becomes greater than the amount of copper to the extent of twenty per cent., when the increase, though larger, about two and seven-tenths cc., again becomes regular.

The effects of cadmium are similar, as shown by the following results, which are also the averages of a large number of experiments, in which the extremes are farther removed from the mean than was found with zinc. As in the preceding experiments the precautions previously enumerated were very carefully observed, except in the case of bulk, in which the variations were identically the same as with the experiments with zinc.

Weight of copper.	Weight of cadmium	Cyanide used.	Increase.
0.05	0.00	10.4 cc.	
0.05	0.01	10.6 "	0.2 cc.
0.05	0.02	10.8 "	0.4 "
0.05	0.03	11.1 "	0.7 "
0.05	0.04	11.6 "	1.2 "
0.05	0.05	12.0 "	1.6 "
0.05	0.06	12.4 "	2.0 "
0.05	0.07	13.5 "	3.1 "
0.05	0.08	14.5 "	4.1 "



These results show that there is a gradually accumulating increase in the consumption of cyanide due to the presence of cadmium. As cadmium is a constituent usually found associated with copper, it must be removed, if reliable results be required. Silver also interferes, but in a regular way. If the amount of silver be known, by previous assay, it is best allowed for by calculation.

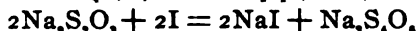
The following modification of the cyanide method has been thoroughly tested, under the immediate supervision of Prof. Seamon, and it is recommended as giving results equal in value to those obtained by the electrolytic method.

The ore is treated according to the method described on page 161 of Furman's Manual of Assaying. In this way a solution of the copper salt is obtained, practically free from lead and silver. This solution is boiled with strips of aluminum foil, resulting in the complete precipitation of the copper together with any silver which may remain in the solution, which is always so small as to be negligible, as I have demonstrated by a number of experiments upon different ores. If cadmium be present, it is only partially precipitated, beginning after the copper is thrown down. If care be taken to stop the boiling, immediately after the copper is precipitated, which can be determined with constant practice, by the eye, the amount of cadmium precipitated is so small as not to cause sensible error. The liquid is decanted from off the aluminum foil and copper, quickly washed several times with hot water, care being taken not to wash away any particles of the copper; three cc. of nitric acid are then added to the flask and boiled to dissolve the copper, the solution is then treated with ammonium hydroxide as in the usual way and titration is made with the usual solution of cyanide.

This method has been very carefully tested and the results were so satisfactory, and nearly uniform, that I recommend it as being as accurate as the electrolytic method, under the conditions in which the latter is usually employed.

The iodide method is most commonly employed in the Lake Superior district and in foreign countries, where it is regarded with much favor. Many chemists regard it as more accurate than the cyanide or electrolytic methods, and there is no doubt

from my experiments that it is more accurate than the ordinary modification of the cyanide and equal to that of the electrolytic. The method depends upon the following reactions :



The best results are obtained when the copper is precipitated with aluminum foil, as previously described under the cyanide method. The method is fully described in Furman's Manual of Assaying, and I only desire to call attention to the necessity for attending to the following precautions :

1. The presence of iron in about equal amounts with the copper requires more "hypo," increasing the amount of copper to the extent of two to three per cent.
2. The solution should be titrated cold.
3. The presence of large amounts of alkaline salts, particularly sodium sulphate, decreases the amount of copper.
4. The presence of bismuth clouds the end reactions.

My experience with the modification of this method, in which the copper is first precipitated with aluminum foil convinces me that with this change the results are as accurate as those obtained with the modified cyanide method; but it is not so rapid, owing to the time lost at various stages; this is an important factor in the adoption of any method for metallurgical work, when thirty and forty assays must be completed every day. The method is a little more difficult to manipulate than the cyanide method

The electrolytic method is perhaps the most highly favored in this country. It has the reputation for greatest accuracy. It requires more time than either of the other, but since it is easy to regulate the work, so that the battery will precipitate during the night, this is not of so much importance. In regular routine work after solution is effected, the copper should be precipitated with hydrogen sulphide, otherwise many interfering metals are apt to be present and deposited with the copper. I have found that errors from this source are largely, if not entirely, eliminated, if deposition be made from a solution containing a large amount of nitric acid. My best results were obtained when I added twenty cc. of strong nitric to about 150 cc. of solution. This holds up the other metals, but a stronger cur-

rent is required to precipitate all of the copper and more attention must be paid to proper and rapid manipulation after precipitation. This method is much improved by previously precipitating the copper from its solution by boiling with aluminum foil and then redissolving the copper in nitric acid. The following results, obtained from the same sample, carefully prepared, obtained by the three methods, furnish a fair idea of the relative values of the several methods.

A copper matte, containing 20.15 per cent. of copper, as determined by a large number of analyses, made by several different assayers, and by different methods, was run by each method. The amount of copper in the second matte, determined from the same data, was found to be twenty-eight per cent., while the per cent. of copper in the ore was 30.18 per cent.

The results obtained by the cyanide method were respectively 20.15 per cent., 27.95 per cent., and 30.20 per cent. The copper was first precipitated with the aluminum foil. The same substances, with the iodide method, first precipitating with aluminum foil, gave, respectively, 20.25, 28.35, and 30.3 per cent. By the electrolytic method, the same substances gave, respectively, 20.045, 28.15, and 30.05 per cent.

These results justify the statement that the iodide method with the aluminum modification gives results usually one-tenth to three-tenths per cent. too high, while the electrolytic method is too high or too low, according to the amount of metallic substances present precipitable by the electric current; and the cyanide method gives results which are practically correct.

## ON THE STANDARDIZATION OF SULPHURIC ACID.

By F. S. SHIVER.

Received February 16, 1895.

M. WEINIG<sup>1</sup> has described a method for the standardization of sulphuric acid by means of weighing the  $(\text{NH}_4)_2\text{SO}_4$  obtained by mixing an accurately measured quantity of the sulphuric acid solution with an excess of ammonia, evaporating, drying, and weighing. His method of procedure is as follows: To an accurately measured quantity of the sulphuric acid solution, ammonia in slight excess is added, the solution evaporated to dryness, dried for half an hour at  $115^\circ$ -

<sup>1</sup> *Ztschr. angew. Chem.*, 1892, 204, 205; *J. Chem. Soc.*, 64, 2, 145.

120° C., cooled in a desiccator, and weighed as ammonium sulphate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). Recognizing the tendency of ammonium salts to decompose, especially when in aqueous solution and in the presence of heat, I was rather uncertain whether, by the mode of procedure just described, one would obtain the normal sulphate. Watts says concerning ammonium salts: "Their aqueous solution, when exposed to the air (still more rapidly when evaporated) generally loses ammonia, an acid salt or a normal salt mixed with excess of acid, being formed; hence, in crystallizing an ammonium salt, ammonia must be added occasionally during the evaporation." I therefore decided to make some experiments in this connection since it was of primary importance that the salt weighed should be the normal sulphate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). Four portions of twenty cc. each of the  $\frac{N}{4}$  sulphuric acid solution were accurately measured out and treated as directed by Weinig.

Results were as follows:

I.	0.3987	gram	sulphur	trioxide	in	twenty	cc.	of	$\frac{N}{4}$	sulphuric	acid.
II.	0.3989	"	"	"	"	"	"	"	"	"	"
III.	0.3990	"	"	"	"	"	"	"	"	"	"
IV.	0.3992	"	"	"	"	"	"	"	"	"	"
Aver.	0.3990	"	"	"	"	"	"	"	"	"	"

These residues tested with delicate litmus seemed to be feebly acid; to further test this point, four portions of twenty cc. each of this same acid were measured out and treated as follows: The acid solution was made alkaline with ammonia in excess and evaporated down to dryness; the dish was then removed from the bath and its contents thoroughly moistened with strong ammonia water, preferably 0.96 sp. gr.; this will avoid the spattering occasioned by the use of concentrated ammonia water and is just as effective as the latter; the dish was then replaced on the bath and allowed to remain until its contents appeared quite dry, then removed and dried for half an hour at 110°-120° C., cooled in a desiccator, and weighed; the drying repeated for another half hour at the same temperature, cooled, and weighed; no further loss of weight occurred from this second drying in these experiments but I think it safer to weigh the second time, else one is left in doubt as to the thorough desiccation of the ammonium sulphate. The results by this method of treatment are as follows:

I.	0.3996	gram	sulphur	trioxide	in	twenty	cc.	$\frac{N}{2}$	sulphuric	acid.
II.	0.4001	"	"	"	"	"	"	"	"	"
III.	0.3993	"	"	"	"	"	"	"	"	"
IV.	0.3992	"	"	"	"	"	"	"	"	"
Average	0.3996	"	"	"	"	"	"	"	"	"

These residues tested with delicate litmus were neutral. It will be seen then that the results by the second mode of treatment are slightly higher in nearly all cases than those obtained by the first method described. In further proof of the slight decomposition that takes place when an aqueous solution of ammonium sulphate is evaporated to dryness, I took one of the residues obtained by the second method just described and added about as much water as there was present in the first evaporation; this solution was evaporated to dryness, dried as already described, cooled, and weighed; the weight of ammonium sulphate before adding water and second evaporation was 0.6591 gram, after adding water and second evaporation 0.6581 gram, a loss of 0.0010 gram ammonium sulphate; the amount of sulphur trioxide calculated from this weight of ammonium sulphate, *viz.*, 0.6581 gram, will be seen to agree quite closely with the results secured by the first method described, in which there seems to be some slight decomposition of the ammonium sulphate.

Therefore from these experiments there seems to be some slight decomposition produced when an aqueous solution of ammonium sulphate is evaporated to dryness and in order to be sure to obtain the normal salt, it is necessary, in my experience, to moisten thoroughly with ammonia water the residue as has been described and then to dry and weigh in the manner directed. The decomposition noticed and the error in results occasioned by it is slight, though the results in most cases are lower than those obtained when precaution is taken to prevent this decomposition by moistening with ammonia water as has been described.

The results of this method compared with the precipitation by barium chloride and weighing as barium sulphate are quite close and satisfactory. In one cc. of  $\frac{N}{2}$  sulphuric acid there was found by the barium chloride method 0.02007 gram sulphur trioxide equivalent to 0.00855 gram ammonia. The ammonium sulphate

method, as carried out by myself, gives 0.01998 gram sulphur trioxide equivalent to 0.00851 gram ammonia. Therefore, one cc. of the sodium hydroxide solution (50.35 cc. of which equals twenty cc. of the  $\frac{N}{4}$  sulphuric acid) is equivalent to 0.003396 gram ammonia by the barium chloride method and by the ammonium sulphate method as carried out by myself 0.003380 gram ammonia.

Another solution of  $\frac{N}{4}$  sulphuric acid was tested by the two methods.

In one cc. of the solution there was found by the barium chloride method 0.01977 gram sulphur trioxide equivalent to 0.008421 gram ammonia.

The ammonium sulphate method, as carried out by myself, gives 0.019895 gram sulphur trioxide equivalent to 0.008474 gram ammonia. Therefore, one cc. of the sodium hydroxide solution (50.25 cc. of which equals twenty cc. of the  $\frac{N}{4}$  sulphuric acid) is equivalent to 0.003351 gram ammonia by the barium chloride method, and 0.003372 gram ammonia by the ammonium sulphate method, as carried out by myself. I think that as a method of standardization the ammonium sulphate method will be found very simple and accurate and for these reasons should commend itself to those analysts who make use of sulphuric acid as their standard acid.

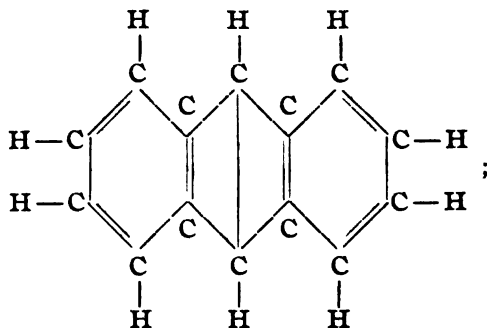
February 11, 1895.

## ON SOME EXPERIMENTS IN THE ANTHRACENE SERIES.

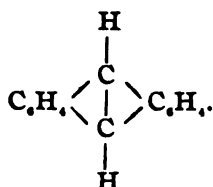
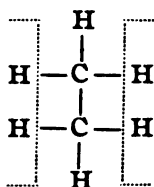
BY C. E. LINEBARGER.

Received March 4, 1895.

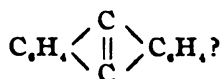
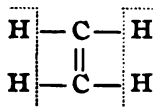
TO anthracene is generally assigned the formula :



it may also be thought of as ethane, in which four of the hydrogen atoms have been replaced by the two bivalent radicals, phenylene:

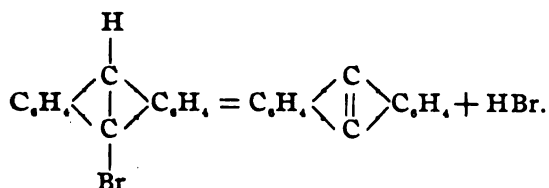


In both the formulas, the two middle atoms of carbon are bound directly together, and the hydrogen atoms in immediate union with them—in the so-called  $\gamma$ -position,—exhibit a characteristic behavior. The question arises, can not the  $\gamma$ -carbon atoms become bound together doubly, so as to form a hydrocarbon, which may be regarded as derived from ethylene,



The question appeared to possess enough importance to merit investigation, and in what follows an account is given of the experiments carried out in seeking an answer to it.

The first attempt to prepare such a compound as the above was made by a study of the action of heat upon mono-brom-anthracene. It seemed likely that through the application of heat hydrobromic acid would be formed by the combination of the hydrogen and bromine in the  $\gamma$ -position, and the bonds of carbon thus set free would unite with each other, as shown in this equation:



Ten grams of pure mono-brom-anthracene were heated in a small round-bottomed flask provided with a delivery-tube. The

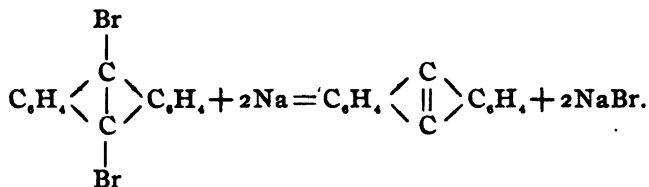
flask was set upon a sand-bath, and its upper part protected from the direct action of the heat by means of a shield of asbestos board. A thermometer was inserted through the cork, reaching almost to the bottom of the flask, so that its bulb was completely immersed in the heated substance. Heat was applied slowly, and it was found that hydrobromic acid gas commenced to pass off at  $250^{\circ}$  C., and the evolution became quite brisk at  $280^{\circ}$  to  $300^{\circ}$ . The temperature was not, however, allowed to rise higher than  $300^{\circ}$ , and when the evolution of gas had nearly ceased, the heating was discontinued. The neck of the flask was full of yellowish crystals, while in its bottom there remained a black resinous mass from which no crystalline substance could be obtained. The crystals were dissolved in hot benzene, and the solution, on cooling, became filled with tablets resembling those of anthracene. These, by a second crystallization from a mixture of alcohol and benzene, were obtained in a state of purity. Their melting-point was found to be  $210^{\circ}$  to  $212^{\circ}$ , which is that of anthracene; they were also, like anthracene, soluble with dark green color in concentrated sulphuric acid; there is no doubt, therefore, that the product of the reaction, that is, as far as anything crystallizable is concerned, is anthracene. The hydrogen necessary for its formation must have been taken from the resinous mass.

Experiments were now carried out on the action of alcoholic potash on the brominated compound of anthracene. Three grams of mono-brom-anthracene were heated with twenty grams of alcoholic caustic potash in sealed tubes at temperatures varying from  $100^{\circ}$  to  $250^{\circ}$ . No reaction seemed to occur at temperatures below  $150^{\circ}$ ; the products obtained at higher temperatures were always about the same. When the tubes, which were always filled with crystals, were opened, considerable quantities of inflammable gases escaped; the crystals, when washed free from caustic potash and purified by crystallizations from alcohol, melted at  $207^{\circ}$  to  $211^{\circ}$ . This point of fusion together with the appearance of the crystals—small glistening tablets possessing fluorescence—and the characteristic green coloration with strong sulphuric acid is sufficient evidence that the product is merely anthracene.



The action of solid caustic potash in like circumstances gave also nothing but anthracene.

An investigation was now made of the action of metallic sodium on di-brom-anthracene dissolved in different liquids. It was thought that, perhaps, the sodium would abstract the halogen from the anthracene compound, and that union would then occur between the two  $\gamma$ -carbon atoms, thus:



A molecule of di-brom-anthracene, together with nearly enough benzene to dissolve it, was sealed up in a tube with somewhat more than four molecules of sodium, and heated at  $100^\circ$  for eight hours; no reaction took place. When heated, however, for the same length of time at  $125^\circ$ , the contents of the tube had turned black. The tube was opened, and the dark-colored crystals purified by repeated crystallizations from mixtures of benzene and alcohol. The crystallizable product finally obtained was nothing else than di-brom-anthracene; the reaction which had supervened had evidently not effected the desired synthesis.

The reaction was now tried with xylene as solvent. Ten grams of di-brom-anthracene were dissolved in sixty grams of xylene—which had been distilled over sodium—and an excess of sodium added. The solution was kept vigorously boiling for twenty hours, an inverted condenser being used. The dark colored products of the reaction were filtered off hot, and the crystals; that soon separated out from the filtrate, repeatedly crystallized out of benzene until a pure product was obtained. This showed itself, by its melting-point ( $207^\circ$  to  $210^\circ$ ), fluorescence, and coloration with concentrated sulphuric acid, to be anthracene. The sodium did, indeed, remove the bromine, but so unstable a molecule was formed that a portion of the product was destroyed in order to yield hydrogen for the formation of anthracene.

The above are the simplest and most direct methods for realiz-

ing the proposed synthesis. Whether others will succeed where these have failed is an open question; at any rate the theoretical importance to be attached to the possibility of existence of such

a hydrocarbon as  $C_2H_4 \begin{matrix} C \\ || \\ C \end{matrix} C_2H_4$ , makes it desirable that all the methods be tried.

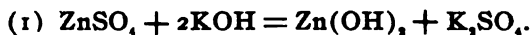
CHICAGO, March 1, 1895.

### ON THE REACTION BETWEEN ZINC SULPHATE AND POTASSIUM HYDROXIDE.<sup>1</sup>

BY C. E. LINEBARGER.

Received March 4, 1895.

It is customary in books on analytical chemistry to represent the precipitation of zinc hydroxide from solutions of its sulphate by means of potassium hydroxide, and its redissolution by the action of an excess of the alkali by these two equations:



These equations are, however, far from corresponding to actuality, and it seems really deplorable that chemists in their desire to formulate compounds and balance equations should, by symbolical representations on paper, give the impression of having duly explained such a reaction as the above, which even a superficial examination shows to vary considerably with the temperature, dilution, and relative masses of the components.

The general scheme followed out in this preliminary study of the reaction of the two salts in question consisted in the addition to a constant quantity of zinc sulphate, varying quantities of potassium hydroxide, the total volume and temperature of the

<sup>1</sup> This investigation was begun in 1888 in the chemical laboratory of the Northwestern University at the suggestion and under the guidance of Prof. A. V. E. Young. It had been the intention to study the reaction between zinc sulphate and potassium hydroxide in a manner analogous to that in which Prof. Young had made "A Thermochemical Analysis of the Reaction between Alum and Potassium Hydrate," published in the Proceedings of the American Academy of Sciences and Arts, June 10, 1885. Only certain preliminary experiments, however, had been performed when I left the University, and the research has not received further attention at the hands of Prof. Young or myself. While these preliminary experiments can be said to be but a small part of the work necessary for the elucidation of the problem of the chemical equilibria presented by the system of zinc sulphate, caustic potash, and water, yet they possess a certain interest, especially for analytical chemistry, which may warrant their being made known.

system being kept constant in all experiments, and the immediate analysis of the precipitate. The details were as follows: 36.2 cc. of a solution containing two grams of anhydrous zinc sulphate were brought into a graduated 500 cc. flask, and diluted to about 225 cc. The required quantity of potassium hydroxide solution was also diluted to about the same volume and added to the zinc sulphate. The flask was briskly shaken, the volume of the mixture made up accurately to 500 cc., again well shaken, so as to insure a homogeneous mixture, and the whole thrown upon a large dry filter. Portions of fifty cc. each of the filtrate were taken and analyzed, duplicate determinations being made of zinc and sulphuric acid, and in some cases of potassium. The sulphuric acid was determined volumetrically by precipitation with barium chloride according to Wildenstein's method, the zinc, volumetrically by precipitation with sodium sulphide, lead acetate in alkaline solution being used as indicator, and the potassium, gravimetrically as potassium sulphate. From the analysis of the filtrate, it is easy, since the total amounts of substances present in the system are known, to calculate the composition of the precipitates.

Before the communication of the results of these experiments, it is well to mention a couple of experiments, designed, one to find out the amount of fixed alkali necessary to just precipitate all of the zinc, the other to ascertain how much was required to redissolve the precipitate. In the first experiment, potassium hydroxide was added, from a burette, to a solution of zinc sulphate of known concentration, until the resulting solution was alkaline, care being taken that the same amount of zinc sulphate and about the same amount of water was present as in the precipitation experiments. It was found that one molecule of anhydrous zinc sulphate is precipitated by 1.62 molecules of potassium hydroxide.

In the second experiment, potassium hydroxide was added from a burette to a solution containing one molecule of anhydrous zinc sulphate until the precipitate, at first formed, redissolved, 13.2 molecules of the alkali being required. In this case, however, the dilution was somewhat different from that in the precipitation experiments.

In Table I are given the results of the experiments :

TABLE I.		
I.	II.	III.
No. of Ex.	Mols. KOH to one mol. $\text{ZnSO}_4$ .	Per cent. $\text{ZnO}$ in precipitate.
1	0.25	17.11
2	0.50	35.10
3	1.00	68.08
4	1.62	100.00
5	2.00	98.49
6	3.00	96.79
7	5.00	89.76
8	7.00	68.87
9	13.20	0.00

If these data be plotted in a curve, the axis of abscissae being the number of molecules of potassium hydroxide to one molecule of anhydrous zinc sulphate, and the axis of ordinates being the per cent. of zinc oxide in the precipitate, it is seen that the curve at first ascends almost in a straight line to ordinate = 100, and abscissa = 1.62 (the point of complete precipitation), and then falls to ordinate = 0, and abscissa = 13.2 (the point of re-solution) in a perfectly regular manner.

### CHEMICAL BRICK FOR GLOVER TOWERS.

BY IRVING A. BACHMAN.

Received January 15, 1895.

IN the last year, Chemical Brick for Glover Towers, from a new locality,<sup>1</sup> have been placed upon the market, which in physical appearance and color are like the famous Blue Welch Brick, and in quality rival them.

Specific gravity, 1.93. Hardness, 7.5.

Color, umber blue. Fracture, blue.

Silica,	$\text{SiO}_2$ .....	72.11 per cent.
Alumina,	$\text{Al}_2\text{O}_3$ .....	20.58 "
Iron oxide,	$\text{Fe}_2\text{O}_3$ .....	5.48 "
Calcium oxide,	$\text{CaO}$ .....	0.92 "
Magnesium oxide,	$\text{MgO}$ .....	0.54 "

A whole brick placed in the bottom of working Glover Tower, acid at 62° B. and 310° F., lost as follows :

<sup>1</sup> Manufactured from the Aiken, S. C., clays.

Weight of brick.....	2934.22	grams.
" " " at expiration of 1 week.....	2933.01	"
" " " " " 2 weeks.....	2931.92	"
" " " " " 3 " .....	2929.41	"
" " " " " 4 " .....	2928.36	"
" " " " " 5 " .....	2927.11	"
" " " " " 6 " .....	2925.26	"
" " " " " 7 " .....	2923.99	"
" " " " " 8 " .....	2922.78	"
" " " " " 9 " .....	2921.53	"
" " " " " 10 " .....	2920.05	"

## Whole brick immersed in boiling

	66° B.	sulphuric acid, 5 hours, lost 0.08 per cent.
Same reweighed	" 60° B.	" " 5 " " 0.07 "
" " "	" 50° B.	" " 5 " " 0.06 "
" " "	" 47° B.	" " 10 " " 0.06 "

## A piece from interior of brick immersed in boiling

	66° B.	sulphuric acid, 5 hours, lost 0.15 per cent.
Same reweighed	" 50° B.	" " 5 " " 0.07 "
" " "	" 50° B.	" " 5 " " 0.07 "
" " "	" 47° B.	" " 5 " " 0.04 "

The edges still remained firm and sharp.

AUGUSTA, GA., January, 1895.

## THE CONTRIBUTIONS OF CHEMISTRY TO THE METHODS OF PREVENTING AND EXTINGUISHING CONFLAGRATION.

BY THOMAS H. NORTON.

[Continued from page 260.]

At about this period several processes were introduced for the preservation of wood against decay; and claims were made that these were also valuable for rendering wood unflammable.<sup>1</sup> These processes consisted essentially in the introduction into the pores of wood of metallic salts in solution, which combined with the nitrogenous matter present to form insoluble, non-fermentable compounds, and therefore removed sources of decay.

The chief methods employed were kyanizing or impregnation with mercuric chloride; burnettizing or impregnation with zinc chloride, using a three per cent. solution; boucherizing or injection of copper sulphate, using a one per cent. solution; and

<sup>1</sup>Rymer-Jones, *Ecl. Eng. Mag.*, 33, 55, 1885.

Beer's process of impregnating with borax. All of these methods give partial protection against combustion. With regard to their availability, expense and the evolution of poisonous vapors, when exposed to heat, militate against the use of corrosive sublimate. Copper sulphate, which can be absorbed to the extent of twenty kgms. per cubic meter of wood, is far inferior to many other salts as a fire protective; it colors the wood blue when exposed to atmospheric conditions, and in common with the mercuric salt, corrodes iron nails and bolts. Zinc chloride is more efficient, although in common with the two preceding salts it affects the tenacity and elasticity of wood. Borax seems to be more free from the objectionable features just enumerated, and more recent experiments have shown that its protective power is far superior to that of the copper or zinc salts, although inferior to that of sodium tungstate and ammoniacal salts.

The operation of impregnation in closed vessels by the use of a vacuum was devised by Samuel Bentham in 1794. It was successfully employed in France by Bréant and Bethel in 1830, and later in England for the purpose of kyanizing and burnettizing, as well as in connection with Payne's process.<sup>1</sup> In boucherizing, the copper sulphate solution is usually forced longitudinally from the butt to the trunk of a tree, just after it is felled, by an ingenious arrangement, involving the use of rubber caps and an elevated tank.<sup>2</sup> •

In 1855 Salomon's process<sup>3</sup> of treatment with aluminum sulphate and calcium chloride, already described in connection with textile fabrics (p. 147) was applied to wood with some little success.

During this same year Maugham's process<sup>4</sup> of treating wood with a mixture of sodium phosphate and ammonium chloride, and Jackson's process, based on the combined use of zinc and ammonium salts, were both submitted to critical tests by Sir Frederick Abel,<sup>5</sup> who found neither as cheap or as efficient as sodium silicate. Abel reported at length to the English Board of Ordnance on the advantages offered by the use of sodium silicate, which he had recommended at an earlier date for use in the

<sup>1</sup> Frémy, *Dict. de Chimie*, 10.

<sup>2</sup> Rymer-Jones, *Ecl. Eng. Mag.*, 33, 55, 1885.

<sup>3</sup> Amer. Arch., loc. cit.

Crimea to render huts fireproof, and which was used in 1856 in camp huts at Aldershot for the Royal Engineers. By applying first a coat of silicate, then a coat of lime, and finally a second coat of silicate, Abel obtained a covering which resisted rain and showed no tendency to crack, shrink, or detach itself from the wood. The cost was one cent for five square feet. Later reports to the board made by Abel in 1870 and 1872 state that the efficiency of this protective was totally unaffected by time. In 1881 he also reports that sodium tungstate, already employed for fabrics, may be successfully used for wood, but that it offers no advantages over the sodium silicate process. It is absorbed by wood at the rate of fifty-six kgms. per cubic meter.

Patera, who studied the subject very extensively, recommended in 1871,<sup>1</sup> the use of magnesium borate for wood, finding it fully equal to sodium tungstate. He urged also very strongly the use of a mixture of one part strong ammonia and two parts gypsum, especially for roofing. Severe tests applied to this protective yielded such satisfactory results that the Austrian Minister of Finance recommended it for all government buildings where woodwork was exposed. Patera also advises the use of a coating of one part of ammonium sulphate, two parts gypsum, and three parts water. Another protective covering recommended by him is obtained by first coating wood twice with a saturated solution of three parts of alum and one part of copperas, and then applying a coat of clay mixed in copperas solution.

The successful use of sodium silicate led to the employment of various siliceous paints. One devised by Vilde and Schambeck<sup>2</sup> seems to have given good results. Its composition is pulverized glass twenty parts, pulverized porcelain twenty parts, pulverized stone twenty parts, quicklime ten parts, waterglass thirty parts. The thick syrup is applied with a brush and hardens quickly.

Ransome's siliceous paint,<sup>3</sup> introduced in 1871, consisted of a mixture of pure quartz and waterglass. After application it was coated with calcium chloride in order to render it perfectly insoluble. It has not been used of late years.

Another process involves the application of three coats of dilute

<sup>1</sup> Loc. cit.

<sup>2</sup> Sc. Amer. Cyclop. of Receipts, p. 217.

<sup>3</sup> Amer. Arch., loc. cit.

waterglass, then of two coats of the same mixed with powdered glass; finally of one of thick waterglass.<sup>1</sup> Other preparations consist simply of more or less dilute waterglass, to which zinc oxide or ferric oxide has been added.<sup>1</sup> A most important modification of the simple silicate is that known as cyanite<sup>1</sup> and prepared by introducing aluminum hydroxide into waterglass, so that it is practically a basic aluminum silicate. It is a perfectly colorless liquid, and is applied with a brush. The cyanite is manufactured in England, and is employed in the English War Department by the Woolwich Arsenal, and by the Department of Railroad Inspection. That the product is variable would be indicated by Helbig's analysis<sup>2</sup> in 1888, when he found nothing present but waterglass.

Among other recent preparations is the ignifuge of Martin<sup>3</sup> of France (1880) used for impregnation, and composed of ammonium chloride fifteen parts, boric acid six parts, borax three parts, water 100 parts.<sup>1</sup> Another French preparation is that of Vendt and Herard,<sup>4</sup> 1885, also for impregnation. It consists of alum twelve parts, borax five parts, sodium thiosulphate three parts, potassium sulphate ten parts, water seventy parts. Somewhat peculiar are the following combinations, also used in France;<sup>5</sup> the first a solution of lead sulphate in neutral tartrates; the second an ammoniacal solution of a mixture of calcium acetate and calcium chloride. Brocher's preparation,<sup>1</sup> manufactured near Dresden, and used to some extent in Germany, is of unknown composition, and involves the use of three different liquids in the course of the application of the several coats. Objection has been made to it for this reason, as well as on account of the tendency of the solutions to solidify before use.

The general recognition of the utility of protective coatings led gradually to the extended use of asbestos. E. G. Erichsen,<sup>6</sup> of Copenhagen, in 1881, devised a new protective which consisted of a soluble silicate, metallic oxides, and lime, with ten to twenty

<sup>1</sup> Boudin et Donny, Rapport.

<sup>2</sup> Archiv. f. Hygien, 1888, 111.

<sup>3</sup> Troost, Bull. de la Soc. d'Encouragement, 1880, p. 384.

<sup>4</sup> Génie civ., 6, 227.

<sup>5</sup> Frémy, Dict. de Chimie, 10.

<sup>6</sup> Amer. Arch., loc. cit.



per cent. of asbestos. It was applied with a trowel and formed a sort of fire-proof enamel which could be washed with water. Erichsen's preparation was extensively used in Europe, both on the continent and in England.

A further step forward was made in 1883, by C. J. Mountford,<sup>1</sup> of Birmingham, England, who brought out a preparation which consisted of asbestos ground and reground in water, sodium or potassium aluminate and waterglass. When liable to exposure to atmospheric agencies, it receives, further, a certain amount of oil driers and gummy matters and sometimes zinc oxide or barium sulphate. The United Asbestos Co., of England, has manufactured this product on a large scale for ten years, and it has been extensively employed, especially in England. Among other important edifices treated with it are the Parliament Buildings, the British Museum, South Kensington Museum, the Crystal Palace, various theaters, Royal palaces, etc. The cost of this material is eighteen cents per kilogram, and 100 kgms. suffice to cover, with three coats, a surface of fifty-four square meters, so that the cost per square meter is about thirty-three cents. It is a thick, gray product, easily applied, presents a satisfactory appearance when used alone on wood, and furnishes an excellent basis for the application of other paints.<sup>2</sup>

This represents probably the best type of protective coating, thus far devised. There are also two other English preparations of some repute, the nature of which is apparently analogous to the above; Bell's asbestos paint and Blane's fire-proof and water-proof paint;<sup>3</sup> while, in America, a single firm manufactures an asbestos paint.

Such is the history of the different methods of restricting the combustion of wood which have been presented during this century.

Let us next note the means devised to test comparatively the value of the diverse materials recommended.

#### TESTS FOR FIRE-PROOF PREPARATIONS.

In Versmann and Oppenheim's extended investigation on protectives for textiles,<sup>3</sup> the study was carried on in such a way as

<sup>1</sup>Amer. Arch., loc. cit.

<sup>2</sup>Boudin et Donny, Rapport.

<sup>3</sup>Report to the British Association, 1859.

effectually to eliminate one after another of the salts experimented upon until a small group was left, the efficiency of each member of which, under varying conditions, was satisfactorily demonstrated. The usefulness of impregnation by sodium tungstate is easily illustrated by exposure to a flame of strips of cotton cloth, some of which have been soaked in a tungstate solution, while others are in the ordinary condition. The merits of the different protectives for wood, as each one in turn came before the public, until a recent date were usually tested by application to a small hut or the like, within which an active fire of very combustible material was started. Such was the custom of Sir Frederick Abel<sup>1</sup> in his series of experiments already referred to.

Some thirty years ago Professor Pepper, of London, made comparative tests on four salts, strongly recommended for impregnating wood, and as a result placed them in the following order, the most efficient first:<sup>2</sup>

1. Ammonium phosphate.
2. Sodium tungstate.
3. Borax.
4. Alum.

The most thorough and valuable study in this field was made in 1887 by two Belgian chemists, Professors Boudin and Donny, of the University of Gand (Ghent) at the request of the Belgian Minister of Public Works.<sup>3</sup> They submitted to rigorous comparative tests all of the preparations then in vogue, some nineteen in number, and it is to be regretted that their exhaustive report has not been reproduced *in toto* in our journals.

P. Lochtin,<sup>4</sup> in 1893, introduced a simple and easy, if not perfectly exact method of testing, which he applied to about fifty chemical compounds, and brought out several interesting facts.

We will consider first his more elementary methods, taking up later the more improved ones of Boudin and Donny.

Lochtin used strips of thick filter-paper fifty cm. long and five cm. broad, which are soaked in solutions of the substances submitted to experiment, usually a series for each substance of five-

<sup>1</sup> Amer. Arch., loc. cit.

<sup>2</sup> Sc. Amer. Cyclop. of Receipts, p. 217.

<sup>3</sup> Rapport sur les procédés destinés à assurer l'inflammabilité des bois, Gand, 1887.

<sup>4</sup> Dingler's poly. Jour., 290, 230.

tenths, one, two, three and five-tenths, five, ten, fifteen, and twenty per cent. solutions of the anhydrous compound. After being hung on lines and drying at ordinary temperature, the lower ends, where greater quantities accumulate, are clipped off. When insoluble precipitates are to be obtained in the paper, it is first soaked in a solution of the soluble salt, then dried, then soaked in a solution of the precipitating reagent, dried, washed, soaked for six to twelve hours in water, washed, and finally dried. The strips are then folded lengthwise, and while held horizontally, with the folds beneath, kindled at one end. Observation then shows whether the foreign substance hinders or helps combustion, and what is the minimal relative weight of a salt or the minimal strength of its solution, necessary to render the paper unflammable.<sup>1</sup>

Experiment indicates that different substances, although in solutions of equal strength, are retained unequally by the paper; the amount retained increasing in proportion to the insolubility or ease of crystallization of a compound. Very soluble substances are absorbed in almost equal proportions. It is also worthy of note that apart from compounds which are practically store-houses of oxygen, as the chlorates, there are substances which distinctly favor combustion, the alkaline sulphates for example. As illustrations of Lochtin's method, a strip soaked in a twenty per cent. solution of sodium sulphate is kindled at one end. It is observed that it burns easily and readily to the end, as readily as if no foreign matter were present. Again, four strips of paper soaked in ammonium chloride solutions, *a* in a twenty per cent. solution, *b* in a five per cent. solution, *c* in a two per cent. solution, and *d* in a one per cent. solution, are in turn held in the flame. No propagation of flame is shown by *a*; *b* shows a small flame, which is extinguished quickly on removal from the source of heat; *c* yields a larger flame, which burns for about five cm. after removal; and *d* furnishes a still larger flame, which burns to the end. It is evident that the use of a two per cent. solution affords partial protection, and of a five per cent. solution, full protection against inflammability. I have found in personal experience an advantage in using for elementary tests the thin slips of pine wood about eight cm. long and one cm. wide, easily

<sup>1</sup> *Dingler's Poly. Jour.*, 290, 230.

obtained from any tobacconist. These are preferable to Lochtin's strips, as they can be used for testing protective coverings as well as solutions; and in the case of the latter the distribution of the foreign substance throughout the strip is more uniform. The experiments conducted before you, illustrate the relative resistance imparted by a number of the preparations already enumerated.

A third method of comparative testing was devised by Boudin and Donny.<sup>1</sup> A cylinder of light iron rods forty cm. long and twenty-five cm. in diameter is mounted upon an horizontal axis so that it can be easily kept in rotation. Beneath this cylinder is a series of five Bunsen burners, consuming 1000 liters of gas hourly. The wood used for the experiments is in the form of rectangular sticks thirty-nine cm. long and fifteen mm. square. After treatment by injection or painting, bundles of four sticks of each preparation—the individual sticks kept apart by light wedges—are attached by wire to the rods of the cylinder, parallel to its axis, and at equal distances from each other. A bundle of sticks which have not been treated serves as point of comparison in each charge of the cylinder. The row of lamps is next lighted, and the cylinder turned at the rate of six revolutions per minute, so that all of the bundles are uniformly and evenly exposed to the action of the flame. The time is then noted at which each bundle takes fire, or is seriously affected by the heat; and when the combustion of a bundle becomes sufficiently active to affect its neighbors, it is removed. As an example of the working of this method the following series of tests may be quoted from the Belgian report:

Wood not treated took fire at the end of one and three-fourths minutes.

Wood treated with zinc sulphate or alum, at the end of three and one-half minutes.

Wood treated with ammonium sulphate or copper sulphate at the end of five minutes.

Wood treated with borax, or boric acid, or Martin's ignifuge, or Brocher's preparation, at the end of eight minutes.

<sup>1</sup> Rapport.

Wood treated with sodium tungstate, at the end of ten minutes.

Wood treated with calcium chloride or ammonium chloride, at the end of fifteen minutes.

Wood treated with waterglass alone, or with lime, or with powdered glass and kaolin, or cyanite, or the Bell, Blane, or United Asbestos Co. preparations, or ammonium phosphate, at the end of thirty to forty minutes.

The two latter were charred throughout without the production of flame.

A still more rigorous and decisive test has been devised by Boudin and Donny,<sup>1</sup> one which places the experimenter as nearly as possible in the conditions which ordinarily precede the outburst of a conflagration; *viz.*, the production of a flame of greater or less intensity in immediate contact with inflammable material; such as happens when an oil lamp is overturned, a box of matches is kindled by the gnawing of an inquisitive rat, or the like.

The test is simple in its nature, and depends, as in the preceding method, upon the use of wooden rods subjected to a protective treatment. A convenient size is that of twenty cm. in length and fifteen mm. square. Thirty-six rods of the same preparation are used to form a small open construction by simply superimposing rows of six alternately crossed upon each other, leaving in the center an open space about six cm. wide for the reception of burning material. The whole arrangement is one permitting of the freest possible circulation of air, a condition which is further aided by placing the construction upon a piece of heavy wire gauze, supported upon two bricks. Little bundles of splints, weighing thirty-five grams each, are used as sources of combustion. They are introduced into the central space, lighted, and the result carefully noted. If combustion be not communicated to the construction by the burning of a single charge, a second is added, and so on. It is easily seen from the series of experiments with these constructions carried on before you, that this method of the two Belgian chemists is of the most searching and exacting nature, and yields comparative results of the highest value.

In such a series of tests, for example, a construction of ordinary wood takes fire at the end of one minute, is in complete combustion two minutes later, and at the end of ten minutes leaves a mass of ashes. Wood treated with ammonium chloride takes fire at the end of three minutes and undergoes complete combustion. Wood covered with cyanite takes fire at the end of three minutes and burns slowly for fifteen minutes, leaving the exterior intact. Wood treated with three coats of waterglass stands exposure to four successive charges of combustible, with but little evidence of the propagation of fire, although the surface of the rods is deeply altered by the exudation and swelling of the silicate. Wood treated with ammonium phosphate, or the United Asbestos Co. preparation, is scarcely affected after four successive charges. The construction remains intact with the interior slightly charred.

#### RESULTS THUS FAR ATTAINED.

Leaving the methods of testing, let us now briefly summarize the results of experiment, and experience with fire protectives up to the present date. For textile fabrics, sodium tungstate and magnesium borate yield, unquestionably, the best results, when materials are to be ironed, while ammonium phosphate or sulphate is preferably used in other cases.<sup>1</sup>

The use of the tungstate, especially, is widespread in England. It may be of interest to know that in the laundry of the Queen's palace, all fabrics of vegetable origin are treated with a solution of neutral sodium tungstate of 28° Tw. containing three per cent. of sodium phosphate. This solution is added to the starch also when the latter is employed.

Abel's researches<sup>2</sup> show that in naval warfare, calcium chloride is valuable to protect rope mantelets, while canvas is well protected by stannic oxide and still better by the double silicate of sodium and lead.

The efficacy of sodium tungstate, as well as of the ammonium salts, for the scenery and decoration of theaters, has also been firmly established.

The comparative results of Lochtin's experiments on pure cel-

<sup>1</sup> F. Fischer, *Ding. Poly. Jour.*, 245, 36.

<sup>2</sup> Amer. Arch., 13 and 14.

lulose<sup>1</sup> may well be summarized here as they offer a valuable classification and furnish useful hints; although it must not be forgotten that the tests were elementary in their nature, and the conclusions, hence, open to criticism, as is, in some cases, evident.

Lochtin divides compounds into three classes, with reference to the effects on combustibles. (1) The *antipyrenes*, which render cellulose unflammable when present in relatively small amounts, and when used in weak solutions. (2) *Indifferent substances* which are effective only when present in large amounts. (3) *Substances which favor combustion*.

### I. ANTIPYRENES.

*Quantities of anhydrous substances required to render cellulose unflammable.*

	Minimal strength of solution used in per cent.	Minimal relative weight (cellulose = 100).
NH <sub>4</sub> Cl	1.5	4.2
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	1.5	4.5
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1.5	4.5
ZnCl <sub>2</sub>	1.5	4.0
CaCl <sub>2</sub>	1.5	4.5
MgCl <sub>2</sub>	1.5	4.5
Al <sub>2</sub> (OH) <sub>3</sub>	1.5	3.8
KAl(SO <sub>4</sub> ) <sub>2</sub>	2.0	..
ZnSO <sub>4</sub>	1.5	4.5
SnCl <sub>2</sub>	2.5	..
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	1.5	8.5
B <sub>2</sub> O <sub>3</sub>	2.5	10.0

### II. INDIFFERENT SUBSTANCES.

HKO	7.5	..
MgSO <sub>4</sub>	7.5	15
NaCl	7.5	35
Na <sub>2</sub> SiO <sub>3</sub>	17.5	50
SiO <sub>2</sub>	12.5	30
KCl	20.0	45
Na <sub>2</sub> HPO <sub>4</sub>	7.5	30
K <sub>2</sub> HPO <sub>4</sub>	20.0	..
Al <sub>2</sub> 3(B <sub>2</sub> O <sub>7</sub> )	12.5	24
AlPO <sub>3</sub>	10.0	30
Ca <sub>2</sub> 2(PO <sub>4</sub> )	12.5	30
MgHPO <sub>4</sub>	12.5	30
ZnB <sub>2</sub> O <sub>7</sub>	7.5	20
ZnHPO <sub>4</sub>	15+	..
WO <sub>3</sub>	10+	15+
Na <sub>2</sub> WO <sub>4</sub>	10+	15+
(NH <sub>4</sub> ) <sub>2</sub> WO <sub>4</sub>	7.5	10+
Clay (air dry)	..	75
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> and KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	7.5-5	..

<sup>1</sup> *Ding. poly. Jour.*, 290, 230.

## III. SUBSTANCES FAVORING COMBUSTION.

$\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SnO}_3$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{ZnCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{FeSO}_4$ .

In reviewing the above tables, it is of importance to note that the aluminum hydroxide used is that obtained by double decomposition between sodium aluminate and sodium bicarbonate. The product formed by the action of ammonia on aluminum sulphate is of no value. It will be seen, also, that the somewhat expensive sodium tungstate is much less effective than many other compounds, the chemical nature of which debars them, however, from ordinary application. Thus, (apart from cost), acid or alkaline reaction, difficulty in solution, hygroscopic properties, or readiness to decompose, on contact with hot iron or otherwise, handicap, as it were, most of the antipyrenes. The chief value of Lochtin's work is to be found in the recognition of aluminum hydroxide as so pronounced an antipyrene and the fixing of the conditions under which it is deposited in the most effective form.

The most important and decisive results with regard to the efficiency of the different current protectives of wood are furnished by Boudin and Donny.<sup>1</sup> Using a classification based upon their rigorous and conclusive tests, we can arrange the protectives in the following series, ascending from the least effective to the most effective.

## I. PREPARATIONS OF LITTLE VALUE.

1. Injection of sodium tungstate (56 kgms. per m<sup>3</sup>).
2. " " copper sulphate 20 " "
3. " " calcium chloride 50 " "
4. " of ammonium chloride 48 " "
5. Coating of waterglass (43 per cent. solid residue), 1 coat, 286 grams per m<sup>2</sup>.
6. Coating of waterglass and zinc oxide, 4 coats, 1 kgm. per m<sup>2</sup>.
7. " " Martin's signifuge, No. 4, 2 coats, 450 grams per m<sup>2</sup>.
8. " " Brocher's preparation, 3 " "
9. " " Blane's asbestos paint, 2 " 1 kgm. per m<sup>2</sup>.
10. " " cyanite (basic aluminum silicate), 2 coats, 450 grams per m<sup>2</sup>.

<sup>1</sup> Rapport.



## II. PREPARATIONS OF SOME VALUE WHICH LESSEN, IN A MARKED DEGREE, THE INFLAMMABILITY OF WOOD.

11. Covering of cyanite, 3 coats, 570 grams per m<sup>2</sup>.
12. " Bell's asbestos paint, 3 coats, 820 grams per m<sup>2</sup>.
13. " waterglass<sup>1</sup> and ferric oxide, 4 coats, 700 grams per m<sup>2</sup>.
14. Covering of waterglass<sup>1</sup> and powdered glass, 6 coats, 900 grams per m<sup>2</sup>.
15. Covering of waterglass<sup>1</sup> (undiluted),<sup>2</sup> 3 coats, 475 grams per m<sup>2</sup>.

## III. PREPARATIONS OF THE HIGHEST EFFICIENCY WHICH PREVENT ALMOST ENTIRELY THE PROPAGATION OF FIRE IN WOOD.

16. Covering of the United Asbestos Co. paint (waterglass, sodium aluminate and asbestos), 3 coats, 850 grams per m<sup>2</sup>.
17. Injection of ammonium phosphate, absorption of 75 kgs. per m<sup>2</sup> after boiling for twelve hours in a sixteen per cent. solution of the salt.

These two protectives would seem therefore the high-water mark of what chemists have attained in their efforts to render wood inflammable. With regard to the permanence of their protective power, it has been observed that, after the lapse of two years, wood treated with the asbestos preparation had lost, in no measure, its resistant qualities, while that injected with ammonium phosphate showed an exceedingly slight diminution in the efficiency. No diminution was noticed at the end of nine months in the resistance of injected wood, kept at ordinary temperature, or at 45° C., or covered with a coat of oil-paint. It should be noted also that the solution of ammonium phosphate does not affect nails and other objects in iron even after contact for several months; also that the solutions of the salt must be nearly saturated in order to yield satisfactory results.

Boudin and Donny's experiments would tend to indicate a

<sup>1</sup> In all these tests a waterglass of forty-three per cent. solid residue was used. It was generally diluted with water, but this additional water is not included in the weight per m<sup>2</sup>.

<sup>2</sup> Wood, when first covered with waterglass, presents a varnished appearance. This is not retained long, as the coating soon begins to scale, and the surface is covered with a white efflorescence.

slight lessening in the strength of wood which has been injected. The general conclusions drawn from their investigations are:

1. The incombustibility of wood, *i. e.*, its non-alteration when under the influence of heat, cannot be attained. It is possible, however, to secure its non-inflammability, so as to preserve ordinarily any structure exposed to an accidental fire, or at least to allow time for the arrival of the ordinary extinguishing appliances, unless it be filled with combustible material.

2. Of the preservative processes used, injection of saline solutions or the application of protective coverings, the former would seem ill adapted for timber of large dimensions, but of manifest value for the less bulky forms of wood. In all such cases the use of ammonium phosphate, in saturated solution, offers such incontestable advantages, that, despite its high price, it should be employed unless excluded absolutely by limitations of expense. (Ammonium phosphate can be obtained for about \$50 per 100 kgms., and as a cubic meter of wood absorbs seventy-five kgms., the cost per cubic meter would be about \$38.)

3. In the majority of cases protective coatings are preferable. The most efficacious is that containing sodium aluminate and asbestos in waterglass, while waterglass alone, or with the addition of aluminum hydroxide, is of great value.

#### EXPLANATION OF THE ACTION OF PROTECTIVES.

Such being the practical results attained, it is of interest for us next to know in just what way these chemical compounds act to prevent inflammability. It is, in fact, a matter of surprise that the experimentation in this field has been so largely empirical, neither preceded nor followed by theoretical considerations.

In studying the effects of heat on ordinary wood, the following will be noted:<sup>1</sup> When exposed for some time to a temperature of 200° C., wood becomes light brown and its strength is materially affected. At 300° it is charred completely, losing all power of resistance, but still without a trace of flame. If, however, the wood be in contact with flame, or be exposed to a red heat, change takes place rapidly, and if air have free access it bursts into flame, and combustion does not cease until the entire mass be reduced to ashes.

<sup>1</sup> F. Fischer, *Ding. poly. Jour.*, 245, 36; Boudin et Donny, *Rapport*.

When wood protected by a suitable coating, such as water-glass, is exposed to a temperature of  $200^{\circ}$  C., it acts exactly as ordinary wood. Wood, however, which has been injected with saline solutions, as ammonium phosphate, is more liable to change. It assumes a deep brown tint, and the resistance to strain is greatly lessened. At  $300^{\circ}$  all forms of protected wood are carbonized, exactly as the ordinary wood, and without flame.

At a red heat, or in contact with flame, prepared wood is completely destroyed; but there is a vast difference between its rate of destruction and that of non-protected wood. At first there is a pronounced period of direct resistance. In cases where external applications have been made, the heat gradually penetrates the protective coating, jets of gas issue through fissures in it, and their combustion contributes to the intensity of the surrounding sources of heat, until, finally, combustion is complete. In the case of wood impregnated with suitable saline solutions, resistance to the flame is likewise marked, but much gas is evolved. This gas is not inflammable but seems, on the contrary, to interfere seriously with the combustion of the surrounding fire. Complete charring is finally reached. It is evident in both cases that the ordinary effects of heat upon wood are seriously hindered or retarded. The first effect of heat, as we have seen, is to produce gas and leave carbon. This gas, if allowed to burn with the oxygen of the air, furnishes a fresh supply of heat to bring about further evolution of gas. But as organic matter and the resultant charcoal are both poor conductors of heat, gasification would proceed very slowly unless the coal on the surface also changed to gas by burning with atmospheric oxygen (as well as by reducing the carbon dioxide and water present), thereby increasing the available temperature. The maintenance of a sufficiently high surrounding temperature must eventually cause the penetration of enough heat into the body of wood exposed to produce complete gasification and carbonization, and finally complete combustion of the charcoal. This action can be retarded evidently by two distinct agencies. The first is the evolution of an inert or non-combustible gas or vapor from the wood through the influence of heat; the second is the presence of an external coating, which is not only a poor

conductor of heat, but also protects the outside zone of charcoal from contact with atmospheric oxygen. It is in one or both directions that fire protectives render service.

The ammonium salts are good types of the first class. Ammonium chloride and ammonium sulphate are readily vaporized and dissociate, the first into ammonia and hydrochloric acid, the second into ammonia, nitrogen, water, ammonium, sulphite, etc. Ammonium phosphate decomposes slowly to metaphosphoric acid (sixty-two per cent. of its weight), ammonia, and nitrogen monoxide. It is probably this slowness of decomposition which renders the phosphate superior to the other ammonium salts. In the case of magnesium chloride, zinc chloride, etc., hydrochloric acid is driven off. In the case of other salts, such as the alums, the borates, copper sulphate, and sodium tungstate, large amounts of water of crystallization are necessarily liberated in the form of aqueous vapor. It is a matter of surprise that this fact, that the storage of considerable amounts of water in the solid form in the interior of wood is a potent factor in the protective value of a number of antipyrenes, should have escaped the attention of chemists. It is an easy matter to calculate the volume of aqueous vapor capable of being formed from a given weight of  $\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$  or  $\text{Na}_2\text{W}_2\text{O}_7 + 10\text{H}_2\text{O}$  or  $\text{K}_2\text{Al}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$ . There is no question but that such salts, as the above, retard the attack of flame chiefly through this agency at first, although after the expulsion of the water of crystallization, the presence of the saline substance coating the charred surface and acting as a poor conductor of heat, as well as preventing the access of oxygen, continues the protection for a certain time. It is in the varying ability of different compounds to form coherent, continuous protective coatings after exposure to heat that we find the reason of the superiority of one composition, for external application, over another. Thus, waterglass alone gives good results. When wood treated with it is heated, we notice a puffing out and swelling, a certain amount of vapor escapes, and the residue is left as a light, voluminous, fairly coherent covering, through which air can penetrate but slowly to the charred surface beneath, and heat is likewise conducted but slowly. The addition of aluminum

hydroxide to the waterglass seems to increase the resistant properties of this envelope, while the further addition of asbestos and the substitution of sodium aluminate for aluminum hydroxide, forming thereby practically a quadruple silicate of sodium, magnesium, calcium, and aluminum, give the highest resistant power.

It may be pertinently inquired, why does the presence of some salts seem apparently to help combustion? Lochtin explains this action<sup>1</sup> by the uneven distribution of some substances during drying or precipitation, more, proportionately, remaining on the surface of the paper or wood used. Here they form porous but slightly compact crusts; and these favor continued glowing or combustion by preventing a loss of heat.

#### PRACTICAL APPLICATION OF THE KNOWLEDGE GAINED.

With this exposition of the results attained in the contest with fire—the fruit almost exclusively of the work of European chemists—what should be the practical application of the knowledge gained to our own conditions in America? It is evident that there should be a rigorous insistence on the use of protective agencies for *all* wood employed in buildings containing material of permanent value, such as deposits of archives, museums, libraries, etc. Equally rigorous should be the requirement in the construction of exhibition buildings; of churches, theaters, and all structures wherein large assemblages are held; of the stands about our fields for athletic amusements; of cars and craft for transportation by land or water; and above all, of the edifices of our institutions of learning.

The applications enumerated above are nearly all easily within the reach of legislative enactment, as they affect the interests or lives of the public.

How far the use of protective agents may be introduced into ordinary construction, and into household equipment it is difficult to say.<sup>2</sup> In England the custom of protecting wearing apparel of vegetable fiber is widespread. No reason exists why American women, earnest in reform, should not advocate a

<sup>1</sup> *Ding. poly. Jour.*, 290, 230.

<sup>2</sup> *Ding. poly. Jour.*, 245, 36.

similar custom here. There is no question, however, but that great stress should be laid upon the wisdom of impregnating the curtains, draperies, and hangings of our homes.

It is to be hoped that the slow burning principle may soon be extended to domestic architecture, but even with our present methods, it is easily possible with the outlay of a few per cent. on the cost of the house to lessen enormously its fire risk. All beams, joists, studding, etc., which are later to be hidden, can be coated during the process of erection. Siliceous coatings can also be applied to all surfaces outside and inside which are ultimately to be painted. Finally, woods to be used for interior finish can be protected by steeping in a solution, preferably of ammonium phosphate, if not of one of the cheaper antipyrenes, before being varnished. Such a house, if isolated, and presupposing the use of wire lath, is practically fireproof in nineteen out of twenty cases of ordinary conflagration. If provided with brick walls and slate roof, the risk is greatly lessened, and it is not difficult to recognize that blocks or districts of such construction are free from *all* danger of conflagration: that, in fact, fire will be confined exclusively to such rooms or houses as may be used for the storage of combustible material. Insurance, under such conditions, approaches almost the vanishing-point; and the freedom of apprehension from loss by fire is not to be measured by dollars and cents. We are here entering upon the proper province of another science. The chemist has provided the means of coping successfully with the dangers of combustion. It is for the economist to insist on the utilization of his achievements, in assuring increased comfort and security to society. Suffice it only to add that existing structures may, to a great extent, be protected especially for those few precious minutes between the discovery of a fire and the arrival of aid, by the generous application of the siliceous compositions to all exposed woodwork. The direct value of such treatment has been promptly recognized in England by a decrease of fifty per cent. in the insurance rates on houses so treated.

#### FIELD FOR FURTHER INVESTIGATION.

Finally, what remains for the chemist to do in this field?

Indirectly he may accomplish much in lessening the fire risk. First in the study of illuminants. Whatever tends to displace the use of petroleum for domestic lighting tends, by so much, to diminish the national fire bill, as this one substance is a most prolific cause of conflagration. It is to be hoped that the way may be opened to an economical and convenient use in this connection of our vegetable oils, now so abundant; or to the introduction of a fuel-gas saturated with hydrocarbons, so safe and economical that it may be promptly accepted for domestic lighting. The possibilities offered in this direction by the extended utilization of calcium acetylide are also most hopeful. Next there is little doubt but that the early approach of the era of cheap aluminum will effect an important revolution in the use of structural materials, the light, unchangeable metal tending to displace wood in many of its external and internal applications. In this field American chemists have taken the lead.

With regard to the production of new protectives it is hardly probable that the last word has been said. We have seen how experiment, beginning with sodium silicate, led successively to the addition of aluminum hydroxide, of lime, of lead salts, of powdered glass, and of finely divided asbestos to the convenient syrupy medium. There is but little doubt that other combinations, less expensive or more effective than those now in vogue, await the experimenter.

The high rank of aluminum hydroxide among protectives, as shown by Lochtin, should lead to extended research with regard to its availability under different conditions, and its most economical application.

The utility of magnesium borate, so warmly recommended by Patera and Fischer, should be definitely established by comparative tests. It is not unlikely that combinations of the borates and silicates may also be found to render good service. Experiments on the deposition of insoluble tungstate in fabrics are also worthy of being carried out.

With regard to protection, by impregnation, it is doubtful whether any better agency than ammonium phosphate can be

found. It would, however, be advisable to study the economical production of this salt for the purpose in question. Might it not be possible to attain cheapness by using successive baths of ammonium sulphate and sodium phosphate; or could not acid calcium phosphate be brought advantageously into the reaction?

A further field of investigation is the possible combination of injection and painting, impregnation with such deliquescent chlorides, as zinc chloride, or magnesium chloride, being followed by a simple external coat of a siliceous paint. Then the most favorable time for injecting or steeping wood with saline solutions should be definitely ascertained. Is it, after completed seasoning, or when the wood is perfectly green, as advocated by Jones?

The question of the most economical combination of protection against fire and of preservation from decay and insect attack, remains also to be settled.<sup>1</sup> Another important phase is the highest attainable efficiency, from the use of salts which store up, in wood, considerable amounts of water of crystallization, such as gypsum; for it must be borne in mind that every volume of solid water of crystallization yields 1700 volumes of aqueous vapor at 100° C.

It is largely along these lines that we may expect to see advance made in the province whose survey we now complete.

In conclusion, let me express the earnest hope that individually and collectively the influence of this Association may be helpfully thrown in favor of any general effort to lessen our tribute to fire. We have made ourselves felt in movements to combat the twin, although antithetic, evils of drought and flood by the preservation and extension of our forests, as well as in other economic directions. Can we not do the same in availing ourselves of the work of Gay Lussac, Fuchs, Versmann, Oppenheim, Abel, Tessier, Patera, and other chemists, by bringing into the American home and the American community that peaceful security and liberation from a dreaded tax, which comes with the practical abolition of danger from conflagration?

<sup>1</sup> Rymer-Jones, *Ecl. Eng. Mag.*, 33, 55, 1885.



# A STUDY OF THE CHEMICAL BEHAVIOR OF TUNGSTEN AND MOLYBDENUM AND THEIR TRIOXIDES<sup>1</sup>.

BY CHARLES HATCH EHRENFELD.

Received March 2, 1895.

## INTRODUCTION.

Group VI of the Periodic System contains a sub-group of more metallic elements—chromium, molybdenum, tungsten, uranium—among the derivatives of which many interesting analogies manifest themselves. Upon comparing the metals themselves, numerous points of interest appear. Thus, beginning with chromium, possessing the lowest atomic mass as well as the highest specific heat, we observe that it oxidizes but slowly when heated in ordinary air. Molybdenum gradually changes under like conditions through its brown and blue oxides until finally it reaches its most stable form, molybdenum trioxide. The same may be remarked of tungsten, although it burns only at elevated temperatures. Uranium, on the contrary, oxidizes at relatively low temperatures. Considering this sub-group as a whole, we can probably detect greater similarities in chemical deportment and analogies in derivatives between molybdenum and tungsten than between the remaining members. To learn more of the behavior of these two metals, to disclose, if possible, differences of conduct while exposed to the influence of the same reagents, is the chief aim of the present investigation. Prefacing the actual study of the metals are some observations upon the deportment of their trioxides which are not devoid of interest, especially as they, in a measure, confirm some earlier observations. The results of this research, while largely of a qualitative character, yet demonstrate quantitative differences between tungsten and molybdenum which serve to define more clearly their position in the Periodic System.

*I. Action of Phosphorus Pentachloride upon Tungsten and Molybdenum Trioxides.*—Persoz and Bloch (*Compt. rend.*, 28, 86, 389) assert that if the anhydrides of inorganic acids be heated

<sup>1</sup> From author's thesis presented to the Faculty of the Department of Philosophy of the Univ. of Pa. for the degree of Ph.D., 1894.

together with phosphorus pentachloride, the products of the reaction will consist of the anhydride and phosphorus pentachloride. They say, for example, that under this treatment tungsten trioxide yields the derivative  $\text{WO}_3 \cdot \text{PCl}_5$ . Hugo Schiff (*Annalen der Chemie*, 102, Heft I) expresses the opinion that in the reaction described, the final products are compounds of equivalent amounts of phosphorus oxychloride with the chlorides of the acids; that tungsten trioxide and phosphorus pentachloride yield a reddish-brown liquid, from which phosphorus oxychloride can readily be distilled, leaving at the same time a reddish-brown residue. The latter, Schiff believes to be tungstyl (or wolframyl) chloride,  $\text{WO}_2\text{Cl}_2$ .

Teclu has made a more recent investigation of this reaction (*Annalen der Chemie*, 187, 255). He finds that as a result of heating tungsten trioxide together with phosphorus pentachloride to  $170^\circ$  in a sealed tube, he obtained tungsten hexachloride. Its solution in phosphorus oxychloride was brown in color.

It seemed to me while engaged in a study of the behavior of tungsten trioxide in vapors of various gaseous compounds, that a repetition of this experiment of Teclu was quite desirable. To this end, equivalent weights of tungsten trioxide and phosphorus pentachloride were intimately mixed, introduced into a porcelain boat, and the latter placed in a hard glass tube contracted at intervals. The air in the tube was expelled by conducting carbon dioxide through it. On applying heat to the boat a white and very volatile crystalline sublimate made its appearance. This was caught at the extreme anterior portion of the tube. Vapors of phosphorus oxychloride were given off, recognizable by their characteristic sharp smell. A brown sublimate next formed beyond the boat. The contents of the boat were reddish-brown in color, melted to a dark red liquid, and gave off reddish-brown vapors resembling those of bromine in color. They condensed to steel-blue colored isometric forms. In every respect they indicated the tungsten hexachloride. A careful examination with a magnifying glass revealed brown needles of the pentachloride distributed around them. These could not be removed, hence the analysis made gave a result that ranges between the theoretical requirements of the penta- and hexa-

chloride. In order to weigh the product and prevent decomposition by contact with air, the tube was sealed at the contracted parts, allowed to cool, and then weighed, after which it was cracked by a hot rod, the contents dissolved out, and the tube refilled with carbon dioxide and reweighed.

0.2562 gram = material.

0.1559 gram =  $\text{WO}_3$  obtained by ignition.

0.1236 gram = W equivalent.

48.25 = per cent. of tungsten obtained.

46.34 = per cent. of tungsten in  $\text{WCl}_6$ .

50.89 = per cent. of tungsten in  $\text{WCl}_6$ .

It may also be observed that the intensity of the heat applied, as well as its duration, had much to do with the quantity of brown material produced. This is not surprising, if the fact be recalled that the hexachloride passes into the pentachloride by ignition in carbon dioxide or hydrogen.

The analysis of another, bright red and more volatile product, showed it to be tungsten oxytetrachloride,  $\text{WOCl}_4$ .

0.0632 gram = material.

0.0423 gram =  $\text{WO}_3$  obtained by ignition.

0.03352 gram = W equivalent.

53.05 = per cent. of tungsten obtained.

53.86 = theoretical per cent. of W in  $\text{WOCl}_4$ .

These experiments were repeated with essentially the same results so that I feel Teclu is justified in asserting that  $\text{rWO}_3 + 5\text{PCl}_5$  give, as direct products, tungsten hexachloride and phosphorus oxychloride. My mode of procedure being somewhat different from that of Teclu will at once explain why in addition to phosphorus oxychloride and tungsten hexachloride, I also got the tungsten pentachloride and oxychloride.

An atmosphere of nitrogen instead of carbon dioxide was tried and gave the same result, but to a less satisfactory degree.

The same method of treatment was also applied to a mixture of equivalent quantities of molybdenum trioxide and phosphorus pentachloride. The reaction took place at lower temperature and was more rapid and energetic than in the case of tungsten trioxide. At first a very volatile white sublimate was deposited in the forward part of the tube, followed by copious brown

vapors. On driving these over gently, a black liquid residue was left in the boat. This solidified, on cooling, forming shining needle crystals which, on examination, proved to be molybdenum pentachloride. Owing to the immediate oxidation in contact with air it was not possible to remove other adhering lower chlorides from the boat, but the latter was at once put into a tube filled with carbon dioxide and thus weighed. The contents of the boat were then dissolved in water and nitric acid and the chlorine determined by titration with tenth normal silver nitrate, potassium chromate being used as an indicator.

0.8296 gram = material.

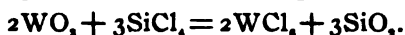
0.51475 gram = chlorine by silver nitrate.

63.25 = per cent. chlorine found.

64.83 = theoretical per cent. Cl in  $\text{MoCl}_5$ .

The low result is accounted for by the presence of lower chlorides which could not be separated.

II. *Action of Silicon Tetrachloride upon the Tungsten and Molybdenum Trioxides.*—Vapors of silicon tetrachloride were passed over tungsten trioxide while the latter was subjected to the heat of a combustion furnace. It was hoped that tungsten hexachloride might be formed according to the equation:



The air was first expelled from the tube by a current of carbon dioxide and then the latter was passed through the small flask containing silicon tetrachloride which was subjected to the heat of a water-bath. No action took place, however, although the operation was continued for about two hours. When a small quantity of air was admitted, tungsten oxytetrachloride and tungstyl chloride were formed.

Silicon tetrachloride was likewise without action on molybdenum trioxide. Rauter (Dissertation, Tübingen, 1893), heated the trioxides together with silicon tetrachloride in sealed tubes. His products were oxychlorides, perhaps in great part due to the presence of air.

III. *Action of Various Gases upon Metallic Tungsten and Molybdenum.* (a) *Action of Nitric Oxide.*—As it was not known whether nitric oxide would have a reducing or oxidizing action it was passed over the metals as well as their trioxides, heat being

applied at the same time. The gas was generated by the action of nitric acid on copper and dried by passing through sulphuric acid. Tungsten trioxide was put into a porcelain boat and the latter into a piece of hard combustion tubing to which heat was applied with one or more Bunsen burners. Nitric oxide gas was passed through the tube and strong heat applied to the boat for half an hour or more. No change was produced on the tungsten trioxide. Molybdenum trioxide treated in a similar way was also unchanged.

Then finely powdered metallic tungsten was placed in the tube, all the air carefully expelled by the current of nitric oxide, and heat applied gradually. At a moderately high temperature (below red heat) action between the metal and nitric oxide began and then proceeded rapidly by means of the heat generated by the reaction, the contents of the boat becoming almost white hot. The product of the reaction was tungsten trioxide.

Metallic molybdenum was subjected to the same treatment. The reaction began only at red heat and proceeded rapidly but with less energy than in the case of tungsten. After continued strong ignition the result of the reaction was not the trioxide but the dioxide of molybdenum.

(b) *Action of Nitrous Oxide.*—Metallic tungsten was placed in the tube and the air carefully driven out of the latter before heat was applied. The action on the tungsten began just as the glass tube began to show signs of redness. The reaction was rapid, with evolution of light and heat, but less energetic than with nitric oxide. Tungsten trioxide was the final product.

Metallic molybdenum, treated in the same manner, required full red heat before any reaction took place. The product was again molybdenum dioxide.

(c) *Action of Nitrogen Peroxide.*—With tungsten, the action began at low temperature, hardly more than  $300^{\circ}$ – $350^{\circ}$ , and proceeded rapidly, but not with the evolution of as much light as with nitric oxide, probably for the reason that the reaction began at lower temperature. Tungsten trioxide was again the product.

With molybdenum the action began at incipient red heat, proceeded with more energy than in the preceding instances, and at once formed molybdenum trioxide.

Considering that nitrous oxide ( $N_2O$ ) shows in its heat of formation ( $-17,740$  Cal.) that it is an endothermic body, and that nitric oxide ( $NO$ ) and nitrogen peroxide ( $NO_2 = -2,045$  Cal.) are members of the same class, it is not surprising that the trioxides of the metals are not in any manner affected by them.

(d) *Action of Sulphur Dioxide.*—Tungsten began to be oxidized at moderately high temperature, but no evolution of light occurred. On continued application of high red heat, only lower tungsten oxides (blue, greenish, and brown) were formed and no trioxide was apparent. A deposit of sulphur was formed on the anterior part of the tube.

With molybdenum, action took place only at the highest temperature, no light being evolved. The oxidation proceeded slowly, and the final product was molybdenum dioxide. Sulphur was deposited on the walls of the tube.

In sulphur dioxide the oxygen is more firmly bound than in any other derivative of these two elements, and yet these metals, molybdenum and tungsten, are capable of withdrawing it.

(e) *Action of Methylamine.*—A current of this gas was generated by heating, in a small flask, a mixture of quicklime and methylamine hydrochloride, the gas being dried by passing over quicklime. The escaping gas was finally conducted into dilute hydrochloric acid. The metals, tungsten and molybdenum, were each heated in this gas. It was thought that a reaction might take place similar to that when metallic potassium is heated in methylamine, namely, the production of the cyanide of the metal. No change, however, took place with the metals, but the dilute hydrochloric acid into which the escaping gas was conducted became charged with hydrocyanic acid. This was undoubtedly produced by the methylamine becoming decomposed in passing through the red hot tube.

IV. *Action of Various Gases on the Tungsten and Molybdenum Trioxides.* (a) *Action of Ethylene.*—Tungsten trioxide heated in a stream of this gas began to be reduced at red heat, the reduction proceeding slowly. Water was condensed on the forward part of the tube, and a mirror of carbon was deposited near the boat. The fact of its being carbon was proved by afterward burning it, no residue being left. After applying heat for about

an hour, a gentle stream of ethylene being maintained, the tungsten trioxide was found to be reduced to a deep blue oxide, quite homogeneous. This oxide was put into an ammoniacal solution of silver nitrate, but after standing more than an hour no metallic silver was precipitated.

Molybdenum trioxide was treated in a similar manner; reduction took place more promptly and readily. A beautiful bronze-brown colored crystalline oxide was left. This was weighed and put into an ammoniacal solution of silver nitrate and digested for some time. The oxide went into solution and metallic silver was precipitated and afterward weighed.

0.0994 gram = weight of material.

0.1538 gram = weight of silver precipitated.

0.0686 gram = corresponding amount of molybdenum,  
according to the proportion :

$2\text{Ag} : \text{Mo} :: 0.1538 : 0.0686.$

69.02 = per cent. Mo in bronze-brown oxide.

70.58 = per cent. Mo in  $\text{Mo}_2\text{O}_5$ .

This result, although not as accurate as could be desired, indicates the brown oxide to be  $\text{Mo}_2\text{O}_5$ .

(b) *Action of Acetylene.*—In a stream of this gas tungsten trioxide was slowly reduced at red heat, a mixture of blue and brown oxides being the result, the latter underlying the former. It may be remarked that in all the reductions and oxidations noticed, the part of the substance near the bottom, or closest to the heat, was most readily acted on, and the reaction most completely carried out.

Molybdenum trioxide was reduced more readily and promptly than tungsten trioxide, and the same bronze-brown oxide was obtained as that from ethylene. Underlying this oxide there was a shining, crystalline, metallic-looking product. In its physical properties it resembled ordinary coke, being light and porous, and easily crushed. A portion of it was put into a silver nitrate solution previously rendered ammoniacal. Metallic silver was precipitated, but there remained black particles undissolved; dilute nitric acid was added and the solution warmed till the silver was dissolved; a black residue was left undissolved. This was filtered out, dried, and ignited on platinum foil; it was completely burned, no ash being left, thus indicating its composition

to be pure carbon. This being the case, it would indicate the probable formation of a *molybdenum carbide*. A quantitative analysis of this material was made as follows: a weighed quantity was put into an ammoniacal silver nitrate solution and gently warmed till metallic silver had separated out. It was then filtered through a weighed filter and dried at  $100^{\circ}$ – $110^{\circ}$ . After weighing, the precipitate was separated, as far as possible, from the filter, and treated with moderately dilute nitric acid and warmed. The silver was dissolved, leaving a black residue of carbon. This was brought upon a dried filter and weighed. Results as follows:

0.1312 gram = weight of "carbide."  
 0.9059 gram = weight of silver and carbon.  
 0.0083 gram = weight of carbon.  
 0.8976 gram = weight of silver by difference.

Calculating the equivalent amount of molybdenum

6 Ag : Mo :: 0.8976 : x  
 x = 0.1329 gram molybdenum.

This gives more molybdenum than the original weight of material, but disregarding this and taking the weights of molybdenum and carbon as found, and dividing by their atomic weights it gives 0.001384 molybdenum to 0.000691 carbon, or two parts molybdenum to one part carbon.

This would indicate a formula,  $\text{Mo}_2\text{C}$ .

Two other analyses were made, only the carbon being determined as above, the molybdenum being taken by difference. Results of second analysis are as follows:

0.0642 gram = weight of "carbide."  
 0.0026 gram = weight of carbon.  
 0.0616 gram = weight of molybdenum.

These results indicate the formula,  $\text{Mo}_2\text{C}$ .

The third analysis was as follows:

0.1255 gram = weight of "carbide."  
 0.0081 gram = weight of carbon.  
 0.1174 gram = weight of molybdenum.

This approximates the formula,  $\text{Mo}_2\text{C}$ , as found in the first analysis. It may be that it is not a definite chemical compound but only a mixture, though the yields obtained at different times



for the foregoing analyses had all the same appearance and physical properties. A further investigation of this compound will be made.

(c) *Action of Methane.*—Tungsten trioxide was heated in methane at the highest heat of a Bunsen burner for nearly an hour with no apparent reduction. The full heat of a blast-lamp was then applied which caused the reduction of tungsten trioxide to the blue oxide,  $W_2O_5$ .

Molybdenum trioxide began to be reduced at the ordinary heat of a Bunsen flame. After heating thus to redness for about half an hour the boat was found to contain both metallic molybdenum and the dioxide, the former being underneath the latter.

(d) *Action of Ethane.*—Neither of the trioxides was affected by this gas, though heated for upwards of half an hour.

(e) *Action of Phosphine.*—Tungsten trioxide was first placed in the tube. Reduction began when the flame had been played under the boat only a few times, so that the temperature could not have been above  $125^{\circ}$ – $150^{\circ}$ . Even before any reducing effect was noticed, a faint white vapor rose from the boat but soon disappeared. The reaction proceeded rapidly, leaving a deep-blue colored product in the boat. A sublimate of phosphorus was formed on the sides of the tube. A portion of the blue oxide was weighed off and ignited to the trioxide in order to determine the percentage of tungsten.

0.0563 gram = weight of material.

0.05645 gram =  $WO_3$  obtained by ignition.

0.04477 gram = corresponding weight of W.

79.52 = per cent. tungsten.

This result seems to correspond to the theoretical 79.70 per cent. of tungsten in the oxide  $W_2O_5$ . In another portion of the blue oxide, phosphorus was determined by digesting with nitric acid, thus converting any phosphorus into phosphoric acid, neutralizing with ammonia, and precipitating with "magnesia mixture." The amount of phosphorus found was only between one and two per cent., indicating that it was probably only mechanically admixed with the oxide. A further confirmation of this is the fact that the sides and edges of the boat were observed to be moist after brief standing in air.

Molybdenum trioxide began to show signs of reduction without any application of heat, and when heat was applied in the gentlest way the reduction proceeded rapidly. As in the case of tungsten a faint white vapor was first formed. There was left a beautiful, lustrous, crystalline product with royal-purple color. A yellow film of phosphorus was formed on the sides of the tube. A portion of the purple oxide was ignited to trioxide with the following result:

0.0452 gram=weight of material.  
 0.0476 gram= $\text{MoO}_3$  obtained by ignition.  
 0.03173 gram=corresponding weight of Mo.  
 70.20=per cent. molybdenum.

This corresponds to the theoretical 70.58 per cent. molybdenum in the oxide  $\text{Mo}_2\text{O}_3$ .

Another portion, treated with nitric acid, was completely dissolved; only 1.99 per cent. of phosphorus was found, hence it could not have been chemically combined, but came from phosphorus that had been deposited on the boat.

Ammonia acts upon both tungsten and molybdenum trioxides more energetically, and the products of the reaction are far more complicated than in the above instances. The less basic character of phosphine compared with ammonia explains the difference.

(f) *Action of Arsine*.—The products were the same blue and purple oxides that were obtained with phosphine, but the reduction took place much more sluggishly. As usual, molybdenum trioxide was the more readily reduced. Much metallic arsenic was formed on the sides of the tube. Only a comparatively gentle heat was applied, owing to the ready decomposability of arsine.

A commonly occurring statement made in regard to the hydrides of nitrogen, phosphorus, and arsenic, is that basicity diminishes with rise of atomic mass; hence it is not surprising that arsine should show the sluggish behavior noted above.

V. *Reduction of the Tungsten and Molybdenum Trioxides by Magnesium, Zinc, and Aluminum*.—(a) *Action of Magnesium*.—Tungsten trioxide and powdered magnesium in molecular proportions were mixed and heated in a small glass tube drawn out

to a point. At a low temperature the magnesium was oxidized with a little puff, light being evolved. A gray to black residue was left. This was digested with dilute hydrochloric acid which left a black or slightly grayish residue. A portion of this was weighed off and ignited to tungsten trioxide in order to determine the percentage of tungsten.

0.0858 gram = weight of material.

0.0928 gram =  $\text{WO}_3$  obtained by ignition.

0.0736 gram = W corresponding.

85.76 = per cent. tungsten.

This corresponds to the theoretical 85.18 per cent. tungsten in tungsten dioxide, thus showing that the trioxide is reduced to dioxide by magnesium.

The reduction of molybdenum trioxide took place in a similar manner, a black residue being left. This was digested with dilute hydrochloric acid and the molybdenum determined by ignition to the trioxide.

0.0386 gram = weight of material.

0.0466 gram =  $\text{MoO}_3$  obtained by ignition.

0.03106 gram = Mo corresponding.

80.48 = per cent. Mo.

This corresponds to the theoretical 80.00 per cent. molybdenum in the sesquioxide, and seems to indicate that magnesium reduces molybdenum trioxide to sesquioxide.

These reductions were also carried out in an atmosphere of hydrogen. At a comparatively low temperature, hardly above  $350^\circ$ , the action between magnesium and tungsten trioxide took place with a little flash of light and the evolution of sufficient heat to crack the combustion tube in which the operation was being performed. The residue was dark gray to black, and looked somewhat metallic. The percentage of tungsten was determined as before.

0.10085 gram = weight of material.

0.1114 gram =  $\text{WO}_3$  obtained by ignition.

0.08835 gram = W corresponding.

87.60 = per cent. tungsten.

This seems to indicate the formation of the sesquioxide which contains 88.46 per cent. of tungsten.

Molybdenum trioxide was reduced at even lower temperature,

with formation of the dioxide as shown by the following analysis :

0.1050 gram = weight of material.  
0.1214 gram =  $\text{MoO}_3$  obtained by ignition.  
0.08093 gram = Mo corresponding:  
77.07 = per cent. Mo.  
75.00 = per cent. Mo in  $\text{MoO}_3$ .

The trioxide obtained by ignition was apparently not homogeneous ; this fact taken together with the above variation from the theoretical per cent. makes the above result more than doubtful. Besides, it is hardly likely that a lower oxide would be obtained by reduction in air than in hydrogen.

(b) *Action of Zinc.*—The experiments with metallic zinc were carried out in the same manner as those with magnesium. Heated in air, in a drawn out tube, the mixture of tungsten trioxide and zinc dust began to react at a moderate heat ( $300^\circ$ – $400^\circ$ ), the reduction proceeding slowly throughout the mass without the evolution of light. The residue was a gray to brown mixture, which the estimation of tungsten indicated to be the oxide  $\text{W}_2\text{O}_5$ .

0.1169 gram = weight of material.  
0.12064 gram =  $\text{WO}_3$  obtained by ignition.  
0.09568 gram = W corresponding.  
81.84 = per cent. tungsten.  
82.12 = per cent. W in  $\text{W}_2\text{O}_5$ .

Molybdenum trioxide mixed with zinc dust and heated was reduced more readily and at lower temperature than tungsten trioxide. The action was also more energetic, being concluded with a little explosive puff. Examination of the residue indicated it to be probably  $\text{Mo}_2\text{O}_3$ .

0.1028 gram = weight of material.  
0.1109 gram =  $\text{MoO}_3$  obtained by ignition.  
0.07393 gram = Mo corresponding.  
71.91 = per cent. Mo.  
70.58 = per cent. Mo in  $\text{Mo}_2\text{O}_3$ .

These two experiments with zinc were then repeated in a current of hydrogen. Tungsten trioxide was easily and gradually reduced at about the same temperature as before. The product was brownish ; analysis showed it to be the dioxide.

0.11295 gram = weight of material.  
 0.1202 gram =  $\text{WO}_3$  obtained by ignition.  
 0.09533 gram = W corresponding.  
 84.40 = per cent. tungsten.  
 85.18 = per cent. W in  $\text{WO}_3$ .

Molybdenum trioxide was easily reduced at low temperature, the reaction taking place with a slight puff. The product was brownish in color. Analysis as follows :

0.1070 gram = weight of material.  
 0.1164 gram =  $\text{MoO}_3$  obtained by ignition.  
 0.0776 gram = Mo corresponding.  
 72.52 = per cent. Mo obtained.  
 70.58 = per cent. Mo in  $\text{Mo}_2\text{O}_5$ ; 75.00 = per cent. Mo in  $\text{MoO}_3$ .

Thus the product seems to be an intermediate one, but this was doubtless caused by impurities. The brownish color of the product suggests, perhaps, that it is the dioxide. If there were an oxide with the composition  $\text{Mo}_4\text{O}_9$ , it would have 72.72 per cent. of molybdenum, which is quite close to the percentage actually obtained.

(c) *Action of Aluminum.*—The trioxides were intimately mixed with molecular quantities of powdered aluminum, placed in a glass tube three or four inches long, sealed at one end, and heated.

With tungsten trioxide there was no action till full red heat was reached when there was a flash and slight report, cracking the tube and scattering its contents. There was not enough material left for analysis, but the walls of the tube were coated with a brownish oxide, probably the dioxide.

With molybdenum trioxide the action was similar, but took place at somewhat lower temperature and was not quite so violent. The sides of the tube were covered with dark blue oxide, probably  $\text{Mo}_2\text{O}_5$ .

These experiments were repeated in an atmosphere of hydrogen but were not successful as no reaction took place. This is undoubtedly for the reason that the temperature required is so high that the trioxides were reduced by the hydrogen before action with aluminum could take place.

At least one interesting fact is brought out by these experiments on oxidation and reduction, and that is that there is a

considerably stronger affinity between tungsten and oxygen than there is between molybdenum and oxygen. This is proved by the fact that in every case the former metal was more readily oxidized while its trioxide was reduced with more difficulty. This is also further illustrated by the experiments with ferric chloride next to be described.

VI. *Reduction of Ferric Chloride by the Metals, Tungsten and Molybdenum.*—A solution of ferric chloride of known strength was made by dissolving piano wire in hydrochloric acid, oxidizing with nitric acid, and evaporating on the water-bath with addition of hydrochloric acid. It was then taken up with water, a few drops of hydrochloric acid added to dissolve basic salts, and the solution, containing 1.11293 grams iron, diluted to one liter.

First a general experiment was made by putting a small indefinite quantity of each metal, in a finely divided state, into an indefinite quantity of ferric chloride solution and a few drops of hydrochloric acid added. The solution containing molybdenum, after standing an hour or so with frequent stirring, lost the yellow color of the ferric salt, hence more was added. The liquid was then largely diluted, a little sulphuric acid added, and a titration made with potassium permanganate to ascertain if reduction of the ferric salt had taken place. A very considerable quantity of ferrous salt was found to be present. The solution containing tungsten stood for several hours but no discharge of color of the ferric salt was noticed. Titration with permanganate however showed a small amount of ferrous salt to be present.

Quantitative experiments were then made to ascertain the relation between the amounts of molybdenum and tungsten and the quantity of ferrous chloride produced. Very small quantities of the metals were taken, as the qualitative experiments showed that the amounts taken for those tests would require a very large amount of ferric solution.

(a) *Molybdenum.*

*First Experiment :*

0.0040 gram = weight of molybdenum taken.

0.01321 gram = metallic iron found by titration.

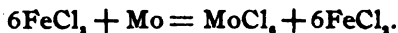
0.01382 gram = metallic iron equivalent to 0.0040 gram Mo.

according to the proportion :

$$\text{Mo} : 6\text{Fe} :: 0.0040 : 0.01382.$$

$$\text{Error} = 0.00061 \text{ gram.}$$

Twenty-five cc. of the ferric solution were used containing 0.02782 gram metallic iron. The molybdenum was completely dissolved. Time of experiment one to two hours. The experiment shows also that 1 Mo is equivalent to 6Fe according to the equation,



*Second Experiment :*

0.00445 gram = molybdenum taken.

0.01566 gram = iron found by titration.

0.01557 gram = iron equivalent to 0.00445 gram Mo.

Error = 0.00009 gram.

All the molybdenum was completely dissolved.

Time, one to two hours.

Twenty-five cc. of ferric solution used.

*Third Experiment :*

0.0867 gram = molybdenum taken.

The action with this larger quantity of metal was very slow, and after standing for about forty hours there was still a considerable amount of metal not dissolved.

*Fourth Experiment :*

In this experiment a more concentrated solution of ferric chloride was used containing 11.4022 grams metallic iron to one liter.

0.07857 gram = molybdenum taken.

0.26702 gram = iron found by titration.

0.27499 gram = iron equivalent to 0.07857 gram Mo.

Error = 0.00797.

That is, only 97.10 per cent. of the molybdenum had gone into solution. This solution stood forty-eight hours and there were still small solid particles to be noticed suspended in the solution.

It seems from the foregoing experiments that complete solution and reduction do not take place in a reasonable length of time, except with small quantities of the metal. The results of the first two experiments are interesting as throwing further

light on the valency of molybdenum, and in suggesting an excellent method for the accurate determination of the atomic mass of this metal as compared with iron.

(b) *Tungsten.*

*First Experiment :*

0.0042 gram = tungsten taken.

0.0007345 gram = iron found by titration.

0.00767 gram = iron equivalent to 0.0042 gram tungsten.

according to the proportion :

$$W : 6Fe :: 0.0042 : 0.00767$$

9.57 = per cent. of tungsten dissolved.

Time, two hours.

*Second Experiment :*

0.00446 gram = tungsten taken.

0.001958 gram = iron found by titration.

0.00814 gram = iron equivalent to 0.00446 gram tungsten.

24.05 = per cent. of tungsten dissolved.

Time, four hours.

*Third Experiment :*

0.00516 gram = tungsten taken.

0.002692 gram = iron found by titration.

0.009422 gram = iron equivalent to 0.00516 gram tungsten.

28.57 = per cent. of tungsten dissolved.

Time, six hours.

*Fourth Experiment :*

0.00475 gram = tungsten taken.

0.005237 gram = iron found by titration.

0.00863 gram = iron equivalent to 0.00475 gram tungsten.

60.69 = per cent. of tungsten dissolved.

Time, eight hours.

These experiments were made with the more concentrated ferric chloride solution. There is seen to be a gradual increase in the amount of iron reduced, roughly proportional to the time; but complete solution of tungsten could not be obtained, although small portions were allowed to remain over forty-eight hours in the ferric solution.

This reducing power of molybdenum and tungsten, indicated in the preceding experiments, is further corroboration of the



experiments made by Smith (*Ztschr. anorg. Chem.*, 1, 360), with these metals and solutions of silver, gold, and mercury salts. It is further additional comparative evidence of the conduct of the metals of this subdivision of group VI. Of the behavior of chromium in this direction we have no experimental evidence, but of uranium it is known that it reduces salts of tin, platinum, gold, copper, mercury, and silver to the metallic condition. With molybdenum the reduction with these metals proceeds quite rapidly, but the speed diminishes with rise in atomic mass, so that the sluggish action of tungsten in ferric salts is not surprising.

## THE DETERMINATION OF SULPHUR IN PYRITES.

A REPLY TO DR. LUNGE.

BY THOMAS S. GLADDING.

Received March 5, 1895.

IN this JOURNAL (June 1894) I published an investigation of the several methods of estimating sulphur in pyrites. As a result of that investigation I rejected all other methods and recommended, in the strongest terms, the general scheme published by Dr. Lunge in his "Alkali-makers' Handbook." At the same time I advised a few minor modifications as conducive to greater certainty and accuracy. In this JOURNAL (March 1895) Dr. Lunge makes a vigorous attack upon each and every one of these modifications. An examination of his paper brings out the important fact that he admits that every modification proposed is accurate in its nature with one single exception. Unfortunately for Dr. Lunge, the single feature selected for condemnation is the one most easily capable of rigid and positive proof as to its absolute accuracy. I shall reserve the consideration of this point and take up in order the modifications to which such strenuous objection is made.

He objects to the use of one gram instead of half a gram. In reply I have found that by my method one gram is as easily handled as one-half gram and double the accuracy is attained in consequence. He objects to the use of a bromine solution instead of aqua regia as a solvent for pyrites. This substitution was made for the reason that quite often when using aqua regia I was annoyed by the separation of free sulphur. Since adopt-

ing the bromine solution I have *never* experienced this trouble.

His first important objection is against my direction to *always* dissolve the ferric hydroxide and test the same for sulphur. He declares that such procedure is unnecessary. On reading his comments on this point, however, we find that he admits that students in his own laboratory have sometimes failed to get out all the sulphur, through imperfect washing. He further "grants that in important cases the ferric hydroxide ought to be tested in some way or another for any sulphur left behind." If the washing out of *all* the sulphur is so absolutely certain as he claims elsewhere, why, it may be asked, does he grant what he does? The concession which he makes is a confession of uneasiness of mind on this very point and is all that I could ask for to justify my own instructions. In answer to his criticisms I will simply state that my washing of the precipitated hydroxide was made exactly as he directs. Five or six washings with hot water, "thoroughly churning" up the precipitate each time has never yet, in my hands nor in those of our assistants, completely removed all the sulphur when using one gram. When using one-half gram the danger of losing sulphur would undoubtedly be much lessened, but no careful analyst will neglect the very simple precaution of dissolving the ferric hydroxide in dilute hydrochloric acid and adding ten cc. of barium chloride to the filtrate.

Lunge's second objection is to my addition of the barium chloride solution, one drop per second, to the boiling sulphate solution. He admits that this method is entirely accurate but tedious and unnecessary, taking "about an hour." In reply I will first state that such addition requires only fifteen minutes, and as it is done automatically from a burette, requires no more labor than it does to "pour it in all at once."

But still further I condemn, as inaccurate, Lunge's method of adding the barium chloride all at once. The following comparative tests made, in part, by our assistant Mr. H. E. Cutts and, in part, by myself personally, are very conclusive on this point. A number of samples of pyrites were treated exactly alike in every respect except in the method of adding the barium chloride.

By slow addition. Per cent.	By sudden addition. Per cent.
50.23	50.84
51.00	51.20
51.00	51.32
51.20	51.50
39.13	39.35
39.40	39.90

In the last three samples the filtrates from the ferric hydroxide were divided into two equal portions, and one portion treated in the first manner, the other in the second. Still further tests were made by dissolving two and seven-tenths grams of chemically pure potassium sulphate in 400 cc. of water, adding five cc. of hydrochloric acid and treating as above.

By slow addition.		By sudden addition.
0.4960		0.4990
0.4960	Theory 0.4965	0.5020
		0.5021

I have also taken two grams of, chemically pure ammonium sulphate, thus imitating more exactly the conditions of the pyrites analysis as carried out by Lunge and obtained

By slow addition.		By sudden addition.
0.4838 gram sulphur		0.4868
0.4828 "	"	0.4900
0.4834 "	"	0.4888

Theory calls for 0.4848. The sudden addition of the barium chloride invariably gives results too high.

I quote the following private communication from Prof. Richards, of Harvard College, on this point. "I am much surprised to find that Lunge is ignorant of the occlusion of barium chloride by barium sulphate. This has been known for a number of decades. In 1890 it was so well known to me that I treated it as a matter of course (*Amer. Acad. Proc.*, 26, 258). This year one of my students has finished a comprehensive work upon this subject showing the amount and circumstances of the occlusion. The paper has already gone to press in the *Proceedings of the American Academy* and the *Ztschr. anorg. Chem.* It wholly confirms your unpublished statements made to Lunge." This is strong testimony corroborating my results given above. My method of avoiding the occlusion of barium chloride by adding the barium chloride solution *drop by drop* and thus insuring the formation of a chemically pure granular precipitate of barium sul-

phate is the same as that adopted by our National Association of Agricultural Chemists in the precipitation of phosphoric acid as ammonium magnesium phosphate.

The last objection of Lunge refers to my method of estimating the 0.20 to 0.40 per cent. of sulphur that may be left in the ferric hydroxide, by the simple plan of dissolving the latter in dilute hot hydrochloric acid, adding ten cc. of barium chloride solution and letting stand over night. This he declares is decidedly *wrong*.

Here again I will quote from Prof. Richards' letter. "This last paper (Dr. Lunge's) seems to me to contain several errors. I think you will find that *in the presence of a considerable excess of barium chloride*, barium sulphate is *not* very seriously soluble in cold ferric chloride solutions, even when acid (see Jannasch and Richards, *J. prakt. Chem.*, **39**, 328-329). Hence your method is as accurate as most analytical methods.

I wish to call especial attention to the method that Lunge has adopted to support his position on this point. He has taken four samples of pyrites and carried them through a complete analysis by his scheme and also by mine and because his method gives 0.20 per cent. more than mine he concludes that I lose 0.20 per cent. sulphur by the solubility of the barium sulphate in the acid solution of the ferric hydroxide. No such conclusion can be fairly drawn from so unscientific a procedure. A far better plan is to divest the problem of all other possibly interfering errors and strip it down to the naked question in hand. This had been done in my first paper as follows:

The insolubility of barium sulphate in the solution of ferric chloride thus obtained was demonstrated by dissolving 0.027 gram potassium sulphate in fifty cc. water, adding five cc. hydrochloric acid and 0.5 gram iron, precipitating hot and allowing to stand over night. We found:

1. Sulphur.....	0.0049 gram.
2. " .....	0.0050 "
3. " .....	0.0051 "

The amount actually present was 0.00496 gram.

I have since repeated the above demonstration by an even more rigid test as follows: I dissolved 0.0135 gram of potassium sulphate in 100 cc. of water, added ten cc. of concentrated

hydrochloric acid, one-half gram of iron, ten cc. of barium chloride solution, precipitating hot and allowing to stand as above. The barium sulphate came down slowly, on cooling. The ignited barium sulphate was snow-white and free from iron, probably on account of its slow formation; I obtained :

1. Sulphur.....	0.0025
2. ".....	0.0026

The amount actually present was 0.00248.

This amount taken in these last experiments corresponds to about 0.20 per cent. sulphur calculated on one gram of pyrites. Lunge claims to have lost this amount on account of the solubility of barium sulphate in acid solution. Were he correct I should have had no precipitate whatever in my experiments above. On the contrary I obtained the whole of the sulphur present to the one-hundredth of a per cent.

To determine sulphur in iron, Troilius, page 38, directs to "dissolve five grams in aqua regia, evaporate to dryness to make silica insoluble. To the filtrate from the silica, which should amount to at least 300 cc., a few cubic centimeters of barium chloride solution are added. After standing one night at the temperature of the room the barium sulphate is completely precipitated." Here we have ten times the amount of iron present that is contained in one gram of pyrites and yet no sulphur is lost. Had Lunge followed the safer and more scientific plan of testing this and also each of the other points in dispute, in the same way that I adopted in my original paper, namely, by working with known amounts of chemically pure salts containing known amounts of sulphur, he would not have fallen into the errors he has.

In conclusion : Of the main modifications proposed by me, Dr. Lunge admits that all are entirely correct, with one exception. The one which he claims to be inaccurate I have incontestably proven to be wholly right. I have also shown that the modification of adding barium chloride, drop by drop, is absolutely necessary to accurate results. I have also shown that the solution of the ferric hydroxide and testing the same for sulphur is certainly the safer course. I conscientiously advise my brother chemists to modify Lunge's method in accordance with my instructions.

## ACIDITY OF GLUCOSE SYRUP AND GRAPE-SUGAR.

BY HORACE E. HORTON.

Received February 18, 1895.

**A**N examination of glucose syrups and grape-sugars will show an acid reaction, and this acidity is due to acid calcium phosphate (rarely), hydrochloric acid, sulphuric acid, and in most instances to sulphurous acid.

The thin liquor obtained by the inversion of starch by acids is strongly acid, and this acidity is reduced by the use of calcium or sodium carbonate to 0.015 gram of hydrochloric acid in 100 grams of liquor.

Acidity due to calcium superphosphate comes from "souring" the bone-black with too strong muriatic acid, when the tricalcium phosphate is broken up with the formation of superphosphate; when a special phosphate black is used in the manufacture of goods, from the occluded superphosphate. I am convinced that in one instance at least, free phosphoric acid had been added to the sample to secure good color.

Sulphurous acid is added to the glucose syrup or grape-sugar when in the cooler.

The acidity is expressed in grams hydrochloric acid or sulphur dioxide in 100 grams substance.

The determination of the acidity was made as follows: 100 grams of glucose or grape-sugar weighed into a beaker and dissolved in about 200 cc. of hot water. A small quantity of carefully prepared delicate litmus solution added, and then titrated with  $\frac{N}{10}$  potassium hydroxide.

I have determined the acidity of a number of American brands with the following results:

CHAS. POPE GLUCOSE CO.

Geneva XXX. 0.0080 sulphur dioxide.

" Jelly 43° Bé. 0.0136 " "

CHICAGO SUGAR REFINING CO.

Confectioners Glucose, 0.012 0.018 0.018 0.018 0.018 0.015 SO<sub>2</sub>.

## AMERICAN GLUCOSE CO.

41° BÉ. Mixing Glucose,	0.0184	0.016	0.019	0.014	SO <sub>3</sub> .
42° " Crystal Glucose,	0.0184	0.0165	0.0205	0.0205	"
43° " Confectioners' Glucose,	0.0184	0.0184	0.0190	0.0184	0.020 "
42° " Brewers' Jelly,	0.0164	0.0164	0.0142	0.0123	"
44° " Export,	0.0172	0.021	0.023		"
42° " Acid Glucose,	0.050	0.048	0.052	0.064	0.0505 "
45° " Export,	0.0225	0.0201			"
" 70" Sugar,	0.036	0.032	0.0279	0.021	0.019 HCl.
	0.016	0.018	0.017	0.027	0.028 "
	0.0295	0.0286	0.032	0.040	0.040 "
	0.045	0.0408	0.043		"

WAVERLY FARM, TOPEKA, KAN.,  
February 14, 1895.

## ASH IN GLUCOSE SYRUP AND GRAPE-SUGAR.

By H. E. HORTON.

Received February 18, 1895.

OF the quantity of ash in glucose syrup and grape-sugar now offered in open market, little is published. Wishing to throw some light on this subject I present figures obtained on analysis of a number of American brands.

The ash determinations were made as follows: Five to ten grams of syrup or sugar weighed in a platinum dish of about 100 cc. capacity, heated with great care until water is expelled, slowly carbonized, and then heated in a muffle at low redness to a finish.

Hydrated grape-sugar, so-called "70" sugar, manufactured by the American Glucose Co.:

Per cent.							
0.536	0.540	0.510	0.510	0.530	0.67	0.31	0.22
0.536	0.540						

Samples of "Special Coloring," American Glucose Co.:

Per cent.		Per cent.
0.31	to	0.52

Samples of "Climax" or "Acme" sugars, manufactured by American Glucose Co.:

"Special dark."	"Dark."	"Light."
0.205	0.16	0.15

"Brewers' sugar," manufactured by Chicago Sugar Refining Co. :

"White."	"Standard."	"Special dark."
Per cent.	Per cent.	Per cent.
0.74	1.00	0.51
0.73	0.72	0.74
	1.15	0.43

"Brewers extract," Chicago Sugar Refining Co., 0.46 per cent.

American Glucose Co., glucose syrups :

	Per cent.		
43° Bé. confectioners' glucose,	0.81	0.33	0.74
41° " mixing glucose,	0.24	0.24	0.26

Chicago Sugar Refining Co. :

	Per cent.		
41° Bé. glucose,	0.14	0.12	0.13
43° " "	1.10	0.65	

National Starch Manufacturing Co., Glen Cove Factory., confectioners' glucose :

Per cent.		
0.80	0.77	0.46

Chas. Pope Glucose., confectioners' glucose, 0.84 per cent.

Peoria Grape-Sugar Works :

41° Bé. glucose,	0.26	0.28	0.26
------------------	------	------	------

The composition of the ash varies with the process of manufacture. If the starch be inverted with muriatic acid and neutralized with sodium carbonate and hydroxide, the ash in finished product will sometimes run over one per cent. and consist almost entirely of sodium chloride.

When oxalic acid is used for inverting and calcium carbonate for neutralizing, calcium oxalate, which is sparingly soluble in glucose solutions, will be found present in glucose, and go over into carbonate on ashing.

When calcium sulphate is used for "brightening" the glucose, a large quantity of it will be present in the ash.

The ash of oxalic acid glucose will contain a small amount of chlorides, coming from muriatic acid used for "souring" the bone, from muriatic added with bisulphite to finished goods in cooler, from sodium chloride by decomposition of calcium chlo-



ride with sodium sulphate after neutralizing, and also from the calcium chloride when the liquor does not receive sufficient sodium sulphate for complete decomposition.

When special prepared phosphate bone is used in the manufacture of syrup and sugar, phosphates are found in the ash. I have found as high as nineteen per cent. of phosphorus pentoxide present.

Iron is present in every ash. It is introduced into the process at the outset and is taken out and as often replaced up to the finish. Batches of glucose made from thin liquor first boiled in a vacuum pan after boiling out with muriatic acid, contain an abnormal amount of iron.

WAVERLY FARM, TOPEKA, KAN.,  
January 20, 1895.

## THE ZIMMERMANN-REINHARDT METHOD FOR THE DETERMINATION OF IRON IN IRON ORES.<sup>1</sup>

BY C. T. MIXER AND H. W. DUBOIS.

Received March 6, 1895.

THE methods chiefly employed in this country for the determination of iron in ores, are the permanganate and Kessler's modification of the old bichromate method (Penny's).

Recently a method has been proposed by R. W. Mahon in the *American Chemical Journal*, 15, 360. The chief feature of this method consists in the proposed use of an indicator solution, for titration with stannous chloride. The indicator solution consists of platinic and mercuric chlorides, the end reaction being indicated by the darkening of the mercurous chloride (formed by the slight excess of stannous chloride), which is caused by the formation of mercurous platinochloride.

As regards this method, it would seem that the frequent standardizations of the stannous chloride that must be made, is a serious objection, and further, the indicator which is used, cannot compare in distinctness with that produced by potassium permanganate.

The objections to the first two methods are mainly those of time consumed in their operation, which specially concerns those who have to make large numbers of determinations. Their general accuracy can hardly be questioned.

<sup>1</sup>This article includes the modifications of the method, as practiced in the Lake Superior iron region.

A preliminary note of the method to be described, appeared in the *Engineering and Mining Journal*, April 14, 1894.

It has been used with most excellent results during the past few years in some of the laboratories on the Lake Superior iron ranges.

The standard works on chemical analysis contain no reference to this method. Furman in his *Manual of Practical Assaying*, page 173, refers rather indifferently to the use of manganous sulphate for titrating in a hydrochloric acid solution with potassium permanganate, but does not seem to be aware of the rapid and accurate method which can be formulated by its use.

Methods have been proposed for titrating directly in a hydrochloric acid solution, but have never proved to be practicable for technical analysis.<sup>1</sup>

The chlorine liberated under such circumstances, seriously affects the results, and it is by the use of manganous sulphate that this is prevented. The use of the above salt for this purpose was first proposed by C. Zimmermann.<sup>2</sup> In this article there is simply outlined the efficacy of manganous sulphate for titrating in hydrochloric acid solutions. Zinc was employed for reduction. A large number of analyses are given, showing the agreement between results obtained from sulphuric acid solutions and hydrochloric acid solutions treated in this manner.

Reinhardt<sup>3</sup> suggested the improvements of reducing with stannous chloride and taking up the excess of the latter, with mercuric chloride, which was then, as now, used in connection with the bichromate method. Later<sup>4</sup> he gives a comprehensive review of the method and suggests a very valuable improvement in the addition of sulphuric and phosphoric acids to the manganous sulphate solution. The addition of the phosphoric acid allows the formation of iron phosphate, which being nearly colorless, renders the end reaction more distinct. Otherwise, the presence of the yellow iron chloride will greatly obscure the end reaction.

The solutions required are as follows :

<sup>1</sup> Löwenthal and Leussen, *Ztschr. anal. Chem.*, 1, 329, and David H. Browne, *J. Anal. Appl. Chem.*, 5, 362.

<sup>2</sup> *Ber. d. chem. Ges.*, 1884 Jahrgang, 15, 779.

<sup>3</sup> *Stahl und Eisen*, Jahrgang, 4, 704.

<sup>4</sup> *Chem. Ztg.*, Jahrgang, 13, 323. The *Journal of the Iron and Steel Institute*, 1889, 1, 400, gives a synopsis of this article and an incorrect reference to it.

*Solution A. Stannous Chloride.*—One pound of stannous chloride is dissolved in one pound of hydrochloric acid 1.2 sp. gr., to which water has been added and, when dissolved, is diluted to two liters.

*Solution B. Hydrochloric Acid 1.1 sp. gr.*—Made by mixing equal volumes of acid 1.2 sp. gr. and water.

*Solution C. Mercuric Chloride.*—A saturated solution is made by dissolving in hot water, allowing to cool and crystallize, and then filtering.

*Solution D.*—One hundred and sixty grams of manganous sulphate are dissolved in water and diluted to 1750 cc. with water. To this are added 330 cc.<sup>1</sup> of phosphoric acid (syrup), 1.7 sp. gr., and 320 cc. of sulphuric acid, sp. gr. 1.84.

This solution permits the titration to be made in a hydrochloric acid solution and thus obviates the deleterious action of the chlorine that is liberated by the action of the hydrochloric acid on the potassium permanganate.

*Solution E. Potassium Permanganate.*—Two hundred and fifty grams of potassium permanganate are dissolved in water and diluted to fill an ordinary carboy (about 44 liters). For more accurate determinations, a solution just one-half this strength is used. For the weight we employ, the main solution has the strength, such that one cc. equals two per cent. This solution is standardized by means of an iron ore, the exact value of which has been ascertained in a number of different ways.

*The Standardization.*—For ordinary commercial work, less than one-half gram of the standard ore is taken, the precise weight being so adjusted that one cc. of the potassium permanganate solution is equivalent to two per cent. of iron. Thus, if the standard ore contain 61.20 per cent. of iron, the weight would be so taken, that the reading of the burette would be 30.6 cc. If, however, it should be 30.7 cc., then either the weight would be diminished in the proportion of 30.6 : 30.7, or one-tenth cc. would be subtracted on all subsequent readings of the burette. The latter is the method generally employed when the discrepancy is so slight as this. For the obtaining of the percentage,

<sup>1</sup> Reinhardt recommends a solution more than twice this strength of phosphoric acid, but we have found the above quantity sufficient.

the burette reading is doubled, after making the correction, if such be necessary.

It will be found conducive to accuracy, and require very little extra work, to accompany each series of determinations by a standard ore, which, being under precisely the same conditions, any error in weight or solutions will immediately be detected.

*The Method.*—About one-half gram of ore (exact weight depending, as shown above, upon the standard ore) is placed in a No. 6 lipless beaker, and two and five-tenths cc. of stannous chloride (*Solution A*) added, this being a sufficient amount for ores analyzing between fifty-five and sixty-five per cent. of iron. It is advisable to use a little less for leaner ores. Then ten to fifteen cc. of hydrochloric acid is added (*Solution B*), and, placing a watch-glass on the beaker, the contents are allowed to boil gently on an iron plate until the ore is completely dissolved.

This will generally require only a few minutes, depending mainly on the character of the ore.

When the ore is dissolved, and while the solution is still hot, additional drops of stannous chloride are added from a burette, until all the iron is just reduced to the ferrous state, which is indicated by the disappearance of the greenish-yellow color.

In case a number of ores are being analyzed, it will be found more convenient to bring several of the solutions up to this point and then slightly oxidize them by the addition of a few drops of the potassium permanganate solution.

In case an excess of stannous chloride has been added originally, the solution is also oxidized as above.

The solution, in its slightly oxidized condition, should be kept warm, and the final reduction be made by a drop or two of stannous chloride. It is desirable to have the least possible excess of stannous chloride, after complete reduction has taken place.

During this operation of reduction and oxidation, the solution is constantly agitated by giving the beaker a rotating motion, which alternates in opposite directions.

The final reduction having been made, the sides of the beaker are washed down and five cc. of mercuric chloride (*Solution C*)

added to take up the excess of stannous chloride, which forms a white silky precipitate of mercurous chloride.

After the addition of mercuric chloride, the contents of the beaker are washed immediately into a 500 cc. beaker, in which has been placed six to eight cc. of *Solution D* and about 400 cc. of water. The solution is now ready for titration.

Ores containing organic matter, some magnetites, and pyritous ores, require the usual precautions. With ores containing very large amounts of organic matter, it is generally most advantageous to burn off directly and follow with the regular method. Ores containing small amounts of organic matter, and pyritous ores, are dissolved in hydrochloric acid and oxidized with potassium chlorate, after which the regular method is pursued.

The use of stannous chloride to hasten the solution of an ore, is particularly convenient in laboratories located in the mining regions. Reinhardt does not mention the use of it. We are not able to state who first proposed its use, but it is not improbable that it may have been accidentally devised independently, by several chemists.

The action of the stannous chloride is doubtless that of converting the iron sesquioxide into the more basic protoxide, towards which the hydrochloric acid asserts a more powerful solvent action.

A tabulation of some results is here given showing the relative rates of dissolving with hydrochloric acid alone, and hydrochloric acid and stannous chloride.

Ore.	No.	Solvent.	Time required for solution.	Iron in Residue.
Soft hematite,	1A	HCl + SnCl <sub>2</sub>	2 min.	0.11
	B	HCl	26 "	0.22
Soft hematite,	2A	HCl + SnCl <sub>2</sub>	4 "	0.09
	B	HCl	35 "	0.12
Specular hematite,	3A	HCl + SnCl <sub>2</sub>	6 "	0.09
	B	HCl	24 "	0.10
Blue granular ore, (Hematite)	4A	HCl + SnCl <sub>2</sub>	6 "	0.18
	B	HCl	30 "	0.21

In order to compare the results afforded by this method with other methods, the following tabulation of analyses has been prepared.

410 THE DETERMINATION OF IRON IN IRON ORES.

No.	Chemist.	Location.	Ore.	Method.	Mixer and Du Bois Zimmer- mann- Per-Reinhardt cent. Method.	
					cent.	Method.
1	B. E. LaLonde,	Pittsburg and Lake Angeline Iron Co.	Lake Angeline Hematite.	Bichromate.	63.40	63.40
2	A. G. McKenna,	Edgar Thompson Steel Works.	Pewabic.	"	64.75	64.80
3	A. G. McKenna,	Edgar Thompson Steel Works.	Toledo.	"	41.30	41.30
4	E. P. Jennings,	Ironwood, Mich.	"	"	61.95	62.05
5	E. E. Brewster,	Iron Mountain, Mich.	Pewabic.	"	63.32	63.38
6	Lerch Bros.	Virginia, Minn.	Mesabi.	Permanganate.	67.44	67.36
7	Porter W. Shimer,	Roston, Pa.	Alabama " fossil ore."	"	48.36	48.25
8	W. E. Hotson,	Iron Mountain, Mich.	Chapin.	Bichromate.	61.87	61.90
9	E. T. Griese,	Mountain Iron, Minn.	Mesabi.	Zimmermann- Reinhardt.	62.19	62.15
9	R. B. Green,	Minnesota Iron Co., Two Harbors, Minn.	"	"	62.12	62.15
9	C. B. Murray,	Edgar Thompson Steel Works.	"	Bichromate.	62.20	62.15
9	E. P. Jennings,	Ironwood, Mich.	"	"	62.12	62.15
9	Lerch Bros.,	Virginia, Minn.	"	Zimmermann- Reinhardt.	62.12	62.15
9	C. A. Buck,	Bethlehem Iron Co.	"	Permanganate, Jones' Reductor.	62.19	62.15
10	Average of seven chemists, Illinois Steel Co.	South Chicago, Ill.	Lake Superior Hematite.	All methods.	67.04	67.02
			Salsbury Hematite.	Bichromate.	62.65	62.70
	" " "	" " "	"	"	61.74	61.80
	" " "	" " "	"	"	61.32	61.30
	" " "	" " "	"	"	61.85	61.80
	" " "	" " "	"	"	59.27	59.30
	" " "	" " "	"	"	61.95	62.00
	" " "	" " "	"	"	62.32	62.40
	" " "	" " "	"	"	61.62	61.70
	" " "	" " "	"	"	62.22	62.30
	" " "	" " "	"	"	62.11	62.10
	" " "	" " "	"	"	62.15	62.20
	" " "	" " "	"	"	62.85	62.80
	" " "	" " "	"	"	61.44	61.30

In numbers 1 to 6, inclusive, our figures were based upon the same standard used by the respective chemist, so that the comparison between the methods is rendered independent of any difference due to the standard employed. All the rest of the analyses were based upon our own standard ore, which represents the mean of a large number of determinations, both by ourselves

and other chemists, involving a variety of modes of standardization.

The merits of the Zimmermann-Reinhardt method may be summed up as follows: (*a*) That the liquid resulting from the solution can be treated directly and without the use of special apparatus. (*b*) The operation of titration is not tedious as in the bichromate method. (*c*) That the simplicity of operation permits determinations to be made with rapidity<sup>1</sup> and without sacrifice of accuracy.

The authors desire to express their obligations to Dr. Harry F. Keller, of Philadelphia, Pa., for valuable suggestions made during the preparation of this paper.

LABORATORY OF MIXER AND DUBOIS,  
ISHPEMING, MICH.

## ON THE MANUFACTURE OF SOLUBLE NITROCELLULOSE FOR NITROGELATINE AND PLASTIC DYNAMITES.\*

J. E. BLOMEN, PH.D.

Received March 16, 1895.

THE discovery that a nitrocellulose could be prepared, which was soluble in a mixture of ether and alcohol, other light hydrocarbons, and in nitroglycerol, gave a start to several industries, of which not the least important was that of the manufacture of nitrogelatine, discovered by the Swede, Alfred Nobel. The use of this substance in the production of celluloid, etc., is of great importance to the industries of this country, but falls outside of the scope of this article.

In order that nitrocellulose should be easily soluble in nitroglycerol it ought to be, as nearly as possible, a pure trinitrocellulose. Higher nitration degrees are insoluble in nitroglycerol, a lower one is fully as unsatisfactory in its action and, therefore, the preparation of this substance is considered one of the most difficult problems encountered in the explosive industry. It is, in fact, considered so difficult to produce, that its manufacture is avoided by explosive companies, they preferring to buy the collodion-cotton made for celluloid manufacturing, at a high

<sup>1</sup> In ordinary practice in our laboratory, determinations can be made in five to ten minutes after the ore is weighed out.

\* Read before the Washington Section, March 14, 1895.

price, in place of running the risk of a failure in manufacturing their own nitrocellulose, although if successful it could be made at a much lower cost.

As a matter of fact, the process of its manufacture is not difficult nor does it require any great chemical skill, but it does require great care in manipulation, uniformity of the materials used, and a never ceasing watchfulness of the details. The cellulose used for its preparation need not be the pure cotton used in the celluloid industry. The inferior article, known in the market as cotton-waste, is quite suitable for this purpose. To be sure the pure cotton is somewhat easier treated and requires less care in the composition of the acids used, but the difference in price between this article and the cotton-waste more than compensates for the additional handling and care. The cotton-waste must, of course, not contain too much fatty matter, but small amounts of organic acids are quite allowable as they are easily removed by suitable washing before using. To do this the bale of cotton-waste is placed in a wooden tank (cedar or best pine wood). I have found that a tank three feet high by five feet in diameter is a convenient size for this purpose. It is now washed, first, with hot water, then with a caustic soda (or sal-soda) solution, about two and one-half pounds caustic soda to a tank full of water, and again thoroughly washed with running hot water. The water having been drawn off, the cotton is taken out and dried, either by hydraulic pressure or by passing it through a centrifugal machine. It is then placed in drying rooms at a temperature of from 75° to 90° C., for at least two days, or until every particle of moisture is driven out. The next process is to pick the dried cotton into a fine fiber. For this purpose a number of cotton-picking machines are constructed and put on the market. They all possess some merits and are indispensable to a large manufacturing plant for nitrocellulose, but require capital to introduce and skilled labor to run, whereas, on the other hand, "hand-picking" is quite satisfactory, does not require initial capital, and labor otherwise wasted can easily be employed. In trying both machine-picking and hand-picking, I have found that the latter gives a more uniform result, and that (on a smaller scale at least) the time of the men waiting



for the nitration of a previous batch can be profitably used for this purpose.

As is always the case, when a number of nitro-derivatives can be obtained simply by using a stronger or weaker nitric acid and by changing the conditions under which it is used, the tri-nitro-cellulose can be obtained in several different ways. The factors to take into consideration are :

- (1) The *proportion* of sulphuric and nitric acids used in the mixture.
- (2) The *strength* of the two acids respectively.
- (3) The *length of time* the acid mixture is allowed to be in contact with the cotton.
- (4) The *temperature* maintained during the reaction.
- (5) The *construction* of the plant itself; and a number of minor conditions, such as the humidity of the atmosphere at the time of the reaction.

In addition to this, there is to be taken into consideration in life, outside of the laboratory, such important items as the cheapness of plant, saving of time and economy of labor. To thoroughly investigate and finally bring each one of these conditions into such harmony that the best and most uniform product at the least expense can be produced is, in itself, a life-work and has not so far been accomplished. I will simply indicate the importance of each one of these questions and then describe *one* way, which I have found, after numberless experiments, to give satisfaction; that is, to produce a nitrocellulose soluble in nitroglycerol at a reasonable cost.

If too *much* sulphuric acid be used this is likely to attack the cotton *before* the nitric acid begins to act, converting it partly into cellulose hydrate (this will later be converted into a higher nitration degree by the nitric acid, as it is much more readily acted upon than the cellulose and will then form an insoluble nitrocellulose) and partly into glucose, which will again partly be nitrated to nitrosaccharose, which is insoluble in nitroglycerol and, besides, a very dangerous substance to have present. Again, if too *little* sulphuric acid be present it will soon form its highest hydroxide and be unable to absorb more of the water rapidly formed during the reaction, when the nitric acid will

become diluted and be unable to nitrate the cellulose. The right proportion of acid mixture is, therefore, of great importance.

If *too strong* sulphuric acid be used the result will be the same as above mentioned for an excess of it; if too strong, or too weak nitric acid be used, it is obvious that a higher or lower nitration degree than the one desired will result. It goes without saying, therefore, that the strength of the acids are of utmost importance.

In the reaction between nitric acid and cellulose no fumes are given off, except what is driven off by the heat (in which it widely differs from several other nitration processes) and although the reaction becomes feebler and, eventually, completely stops, when the acid has been diluted to a certain limit, it only gradually diminishes in force, and therefore the time has to be so balanced that the lower nitration degrees have been passed without part of the cellulose having been too highly nitrated, when it is stopped. Hence the importance of careful regulation of the time.

If the nitration pots are surrounded with water kept at a constant temperature, it will be found that the quickness and degree of the nitration depends, to a considerable extent, upon the temperature of this water. Thus, if the temperature be kept up to a high degree the nitration will be much more rapid, but at the same time experience has shown me that, in this way, a *mixture* of different nitration degrees is much more apt to result, than the uniform nitration from one degree to another. Curiously enough, the same result is obtained if no external heat at all be applied, and accordingly in my experience a carefully maintained temperature of 70° C. has been found to give the most uniform result, but no doubt good, and perhaps more economical results can be reached by elevating the temperature of the surrounding water.

It is within the experience of every chemical manufacturer, how much the size and construction of the vessels, in which the reaction takes place, influence the result, and this is fully as true in this industry as in any other. It is especially so as the cotton is so bulky that it is hard to keep every part of it in contact with the acid mixture. Under otherwise the same conditions, I have found quite a difference in the product when it was made on a

clear and dry day, and when the day was rainy or cloudy, the more so, as the building in which the operation takes place has to be left open to a great extent to allow the acid vapors to be carried away.

Even in very large dynamite works it is not always practicable to adopt the very best appliances for the manufacture of nitrocellulose, because it must necessarily be only a small part of the plant, (an average of two per cent. of the ingredients) and can only be conducted by dependence for labor, material, etc., on other parts of the works. In a large plant for the exclusive manufacture of this kind of nitrocellulose the conditions would be more favorable for improvements.

The acid mixture I have found best to use is the following: Nitric acid of 1.430 sp. gr., free from chlorine and such an amount of sulphuric acid as would influence the specific gravity, forty parts; and sixty parts of sulphuric acid of 1.835 sp. gr. The specifications for acids governing the supply for other parts of the works can be adopted for this. It is self-evident that this proportion of acids is only necessary when the work is carried on as hereinafter described and can be greatly varied under different conditions. Such an acid mixture as this cannot be stored in iron drums for any length of time and is therefore troublesome to get, if the nitric acid is not manufactured at the works. The nitric acid must be shipped in carboys; the sulphuric acid can be shipped in drums.

In mixing the two acids a sufficient quantity can be mixed at one time to last for two or three days' supply, and then stored in drums, as the acid will hardly, in this short time, affect the iron to any great extent. The mixing is best effected in a wooden tub lined with heavy lead in such a way as to allow a water-jacket of about two inches around it. (A condemned nitroglycerol apparatus with the coils removed answers this purpose very well.) If compressed air be at hand this should be used as a stirrer by placing a small perforated lead coil at the bottom of the tank and letting the air bubble through the mass since it is very difficult to get any other kind of stirrer that will stand the acids. The men should be warned to have the earthen-ware faucet at the bottom of the tank well greased, to tap it very

gently, to always use their rubber gloves and to have an ample supply of water close at hand.

This mixture although carefully made from acids of 1.430 and 1.835 sp. gr. respectively, will vary in specific gravity from 1.678 to 1.682, but if below or above this, some mistake has been made in the mixing or stirring. The nitric acid should always be dumped in the tank first and the sulphuric acid afterwards so as to give the latter a chance to mix by gravity as much as possible. Just before using, the acid mixture should be stirred again. For this purpose it is convenient to have a lead-lined tank, with an air-stirrer, of a size to hold one charge for the nitrating pots in use, in which the mixture is stirred up thoroughly and then drawn off for each pot as rapidly as possible.

The arrangement of the nitration pots, of course, must depend on existing conditions, such as size and form of the building, the size of the pots, the material used for confining the water around them, the supply of water of suitable temperature, etc. Under ordinary circumstances I have found it practicable to use earthenware pots sixteen inches deep and thirteen inches in diameter, enclosed in wooden troughs twenty feet long by twenty inches wide, connected by means of leaden pipes. If shorter it is a waste of lumber, if longer they are likely to leak from the pressure. If the troughs can conveniently be made from concrete or brickwork with water-tight mortar, of course it can be extended to any desired length.

Experience has shown two pounds to be the right amount of cotton to be used in one nitration pot. To save time and labor it is important to nitrate as much as possible at one time, but the necessity of getting a uniform product limits the amount, and as the cotton clogs or packs together as soon as wet by the acid mixture, only so much can be used at one time as will allow the mixture to act uniformly on the whole bulk of the cotton, without nitrating the outer portion too much and the inner portion too little. After having tried different amounts I have reached the conclusion that (under the given conditions) two pounds is the maximum that can safely be treated in one nitration pot.

Forty-five pounds of the well-stirred acid mixture is weighed

out and placed in the pots, which are surrounded by water heated to  $70^{\circ}$  C. The two pounds of cotton for each pot should be previously weighed out, and ready to be put in so as to have this done as nearly simultaneously as possible. It is now immersed in the acid mixture, turned about a few times with a fork and kept down by a perforated cover. The only reason for using such an excess of acids is that the cotton must be covered by it—if good covers are used forty pounds or less is enough. Besides the perforated covers, each pot should be provided with solid overlapping covers to keep back the fumes. It is now left for one hour and ten minutes, except that after thirty-five minutes the cotton is quickly turned about with the fork, a couple of times and the covers replaced. After this the nitrated cotton is quickly taken up, squeezed with the fork, and wrung out in a centrifugal machine. From this it is taken to a large-sized tank well filled with cold water, where it is thoroughly washed. It should be kept in this tank in running water for about one hour. It is well to have a large quantity of water to prevent heating by adherent sulphuric acid, but it is not so important as in the case of guncotton, because it is not so easily ignited by the heat generated nor is the acid as strong as in the latter case. It is then transferred to another tank of the same size. This is conveniently placed below and the nitrocellulose transferred on a wooden slide. Here it is washed in a sal-soda solution. From this it is taken to a pulping machine or hollender, where it is reduced to a fine pulp. This part of the process is of the greatest importance as it has been proven time and time again that if insufficiently pulped it is hard if not impossible to dissolve it in nitroglycerol. I have found that nitrocellulose, which had before been rejected as insoluble, worked very well after it had passed two or more hours in the pulp-machine. From the pulp-machine it is emptied into a large tank, allowed to settle, and the water filtered off. It is then passed either through a centrifugal machine or a hydraulic press, and thus freed from water as far as possible. It is spread in drying boxes to a depth of about two inches and kept at a temperature of about  $80^{\circ}$  C. till thoroughly dried. After that it is rubbed through fine screens until as fine as the finest flour. If treated in this way the nitrocellu-

lose will dissolve very quickly in nitroglycerol. Seven per cent. of nitrocellulose dissolves in ninety-three per cent. nitroglycerol in less than twenty minutes to a transparent jelly and three and five-tenths per cent. gives the nitroglycerol the consistency of syrup. Several hundred analyses of nitrocellulose prepared in this way show it to contain from 20.5 to 21.8 per cent. of  $\text{NO}_2$ , which very nearly corresponds to the formula of trinitrocellulose. The process carried out in this way is simple and requires no great skill or experience. The cost under ordinary circumstances and with conscientious supervision varies between thirty-five to forty cents a pound. The spent acid must of course be taken care of either by regaining it or by using it direct for other chemical processes. The only laboratory facilities that are absolutely needed are three different hydrometers, one thermometer, and a specific gravity jar—provided the acid contractors are honest.

If the nitric acid be made at the works there is no difficulty in economizing by using the lower grades made up to strength, from the acid for nitroglycerol manufacture, for instance, or from other high grades. If properly and constantly tested the waste nitroglycerol acids can be made up to strength if sufficiently strong nitric and sulphuric acids are on hand. A good and attentive chemist is certain to be able to use the products from other parts of the works (nitroglycerol works, regaining works, acid works, etc.), in such a way as to accomplish a considerable saving in the price above quoted of nitrocellulose. The conditions and facilities for making it differ, but it is safe to say that the makers can save from ten to twenty-five per cent. of the cost of manufacture in the above way by the employment of a competent chemist, to say nothing of what they save by not buying the collodion-cotton of the market at \$1.00 a pound.

The best way to test the nitrocellulose for efficiency in the laboratory is undoubtedly by trying its solubility in nitroglycerol under the same conditions as prevail in the works, next to that is to note the time and result in dissolving it in an ether-alcohol mixture, and finally to use Lunge's nitrometer. The last test, though of less direct practical value, will enable the chemist to obtain a pretty good idea of what he is making and a well-

kept record of all these tests is sure to soon make it possible to always turn out a uniform product—the great desideratum in all chemical industries. The laboratory method of testing, and analysis of materials for, and products of this industry are so simple that they need not be mentioned to an assembly of chemists.

COLUMBIAN UNIVERSITY, February, 1895.

### NEW BOOKS.

**ELEMENTS OF QUALITATIVE AND QUANTITATIVE CHEMICAL ANALYSIS.**  
By G. C. Caldwell, B.S., Ph.D. Third Edition, Revised and Enlarged.  
pp. 187. Philadelphia: P. Blakiston, Son & Co. Price, \$1.50.

Dr. Caldwell has made several changes in this third edition which increases the value of a book which already had much to recommend it, as the writer can testify, having used it in the laboratory for two years. Nitroso  $\beta$ -naphthol is added as an additional test for nickel and cobalt. It would seem as though more tests might be added for the basigens, with advantage to the student. On page 15, the equation for the oxidation of oxalic acid by potassium permanganate is not correct in this, as it was not in the former edition. The marks  $\sim$ ,  $\sim$ , to indicate respectively "precipitate" and "gaseous product," so far as we know entirely original with the author, are great aids to the instructor in the class-room drills. The discussions in Part I on the processes of analytical chemistry are particularly valuable, while the preliminary discussions preceding the schemes, on "the chemistry of the work" are an excellent feature. Lawrence Smith's method for alkalies is added in this edition. While the portion devoted to quantitative analysis is necessarily abbreviated in a work of this character, sufficient space is given to allow students of limited time to get a very good general knowledge of the methods employed. But we would like to have seen the determination of potash added to those of phosphorus pentoxide and nitrogen, for those interested in agricultural analysis.

ALBERT H. WELLES.

**ELEMENTARY QUALITATIVE CHEMICAL ANALYSIS.** BY FRANK CLOWES, D. Sc. LOND., AND J. BERNARD COLEMAN. pp. 180. Philadelphia: P. Blakiston, Son & Co. Price \$1.00.

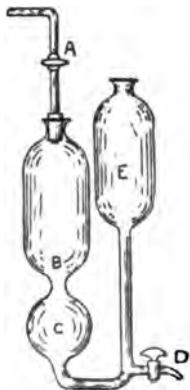
The reviewer fails to discover any important improvements in the arrangement or matter in this book upon others of the same

class. A good deal of space is devoted to directions for manipulation, preparation, and preservation of apparatus. Part of it is given to simple experiments usually included in other books than one intended for qualitative analysis. The methods for working with the blowpipe are far from being full. The tables are the same as ordinarily seen in books on qualitative analysis and present no feature for especial comment. The clumsy terms *mercurosum* and *mercuricum* are employed. Needless and misleading abbreviations, as HA for  $C_2H_3O_2$ , are used. The neatly bound book has a good index and is well printed.

CHAS. BASKERVILLE.

### NOTES.

*A New Hydrogen Sulphide Generator.*—The accompanying figure shows a hydrogen sulphide apparatus in which objectionable features are reduced to a minimum, and the greatest convenience secured. At B is a perforated disk of lead, glass, or porcelain which supports the ferrous sulphide. When the stop-cock at A is closed, the acid is forced back by the gas into the vessel E. The globe C receives the excess of gas and prevents its bubbling back into E. When the acid is exhausted, it is drawn off at D and a new supply is added above.



The advantages of the apparatus are as follows:

1. It is in one piece.
2. The pressure is small when the cock is closed.
3. The quantity of escaping gas is reduced to a minimum.
4. It is conveniently filled and emptied.
5. It is always ready.

The apparatus is attached to a suitable support. It may be made of any size. The one now in use in the laboratory of Cumberland University has vessels and globe eight centimeters in diameter. It was made for me by Messrs. Eimer and Amend, New York, and is giving entire satisfaction.

CUMBERLAND UNIVERSITY.  
LEBANON, TENN.

J. I. D. HINDS.



*Molybdenum Carbide*.—Under date of April 4th, Mr. C. H. Ehrenfeld sends the following additional information upon the supposed molybdenum carbide (see page 388 of this issue):

"Further investigation of the supposed molybdenum carbide has shown that it is undoubtedly only a mechanical mixture. Analyses of different yields of material gave no concordant results. The amount of carbon present seems to depend very largely upon the conditions under which the compound is obtained. For example, when the operation is conducted slowly, at the comparatively low temperature of a Bunsen burner, the percentage of carbon is much greater than when the material is obtained by using the high heat of a blast-lamp."

*The Gas contained in Uraninite* is, according to Profs. Ramsay and Crookes (*Chem. News*, 71, 151), a mixture of helium and argon with a little nitrogen. Prof. Crookes' measurements of the helium line give, as the wave-length, 587.45, while according to Angstrom the wave-length of the helium line is 587.49, and according to Cornu 587.46. In this connection the following extract from Hillebrand's paper describing the occurrence of nitrogen in uraninite is of interest (*Am. J. Sci.*, [3], 40, 384).

"The nitrogen is set free from the mineral as nitrogen gas by the action of a non-oxidizing inorganic acid, and by fusion with an alkaline carbonate and probably also caustic alkalis in a current of CO<sub>2</sub>. As obtained by the use of acids the gas is colorless, odorless, a non-supporter of combustion, unchanged by mixture with air, neutral to litmus papers, not absorbed by caustic alkalis, and insoluble in water, at least its coefficient of absorption is so small as to be inappreciable without elaborate experimentation. When subjected in a eudiometer to the ordeal described by Bunsen<sup>1</sup> there results no alteration in volume, other than that caused by the union of the hydrogen and oxygen added.

This evidence, while fairly conclusive as to the nature of the gas, was purely negative, and proof of a more positive character was sought. Nitric acid is formed from a moist mixture of the gas with pure oxygen by long continued passage of the electric spark, and ammonia is produced by the so-called silent discharge

<sup>1</sup> Gasometrische Methoden, 2d ed., pp. 73 and 74.

through a mixture of the gas with three volumes of electrolytic hydrogen. The contraction produced in the latter case could be measured by cubic centimeters, and water used as an absorbent of the ammonia colored red litmus paper deep blue, besides giving a strong ammonia reaction with Nessler's reagent. With dilute hydrochloric acid as an absorbent there was obtained an abundant precipitate of ammonium platonic chloride. In a Geissler tube under a pressure of  $10^{\text{mm}}$  and less the gas afforded the fluted spectrum of nitrogen with great brilliancy." \* \*

"Throughout the whole list of analyses in which nitrogen has been estimated the most striking feature is the apparent relation between it and the  $\text{UO}_2$ . This is especially marked in the table of Norwegian uraninites recalculated, from which the rule might almost be formulated that, given either nitrogen or  $\text{UO}_2$ , the other can be found by simple calculation. The same ratio is not found in the Connecticut varieties, but if the determination of nitrogen in the Branchville mineral is to be depended on, the rule still holds that the higher the  $\text{UO}_2$ , the higher likewise is the nitrogen."

*Compounds of Argon.*—Berthelot finds that argon combines with the vapor of benzene under the influence of the silent electric discharge giving a yellow resinous odorous substance condensed on the surface of the two glass tubes between which the electric action is exerted. This substance, when heated, is decomposed, leaving a bulky carbonaceous residue. The volatile products of decomposition turn litmus blue, indicating that an alkaline substance is contained in them. (From a translation of Berthelot's article in the *Chem. News*, 71, 151.)

**ERRATA.**—In Professor Venable's article in the February number the name of Victor Meyer occurs in several places. It should read Lothar Meyer.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

---

### GERHARD KRÜSS.

Received April 4, 1895.

THE death of Professor Krüss at the early age of thirty-five, and in the midst of a career already remarkably brilliant and fruitful, will be keenly felt by all, and especially by those who have known him as teacher and friend.

He was born at Hamburg on the 14th of December, 1859, his father being the well-known optician A. Krüss. In 1879 he went to the University of Munich and entered upon the study of chemistry with Baeyer and Zimmermann as his teachers. The summer semester of 1881 he spent at Heidelberg studying under Bunsen.

His early acquaintance with physical instruments, and especially with the spectroscope, led Krüss to a series of investigations, begun while he was yet a student, in the field of spectroscopic chemical analysis. In his first paper, which appeared in 1882, he described a method for ascertaining, by means of the spectroscope, whether two colored solutions, when mixed, act chemically upon each other or exist together unchanged. Pursuing this question still further he obtained the interesting results which are recorded in the series of articles upon "The relation between the composition of organic compounds and their absorption spectra," wherein he proved by many measurements of the absorption bands of indigo and fluorescein and their derivatives that the introduction of methyl, oxymethyl, ethyl, or bromine in the place of an atom of hydrogen moved the absorption in the spectrum towards the red, while the introduction of a nitro

or amido group had the opposite effect. Krüss saw and clearly described the practical bearing of these discoveries, and as a result the spectroscope is now employed at Höchst, both for the examination of the purity of known dyes and as a guide to the production of new ones.

Krüss was also greatly interested in the application of the spectroscope to quantitative determinations, his researches upon this subject being largely recorded in the book which he and his brother, Hugo Krüss, published in 1891—*Kolorimetrie und Quantitative Spektral-analyse*. In 1892 appeared his book upon the use of physical methods in chemistry, entitled *Spezielle Methoden der Analyse*.

Krüss's first strictly chemical researches were taken up under the able guidance of Clemens Zimmermann, at whose suggestion he undertook the investigation of the sulphur compounds of molybdenum, thus continuing the studies in the chromium group which Zimmermann had so brilliantly begun by his researches upon uranium.

After the death of Zimmermann (March, 1885) Krüss turned his attention to the study of the compounds of gold. In these investigations, which extended from 1886 to 1893, he corrected the older statements concerning the gold oxides, showing that only  $\text{Au}_2\text{O}$ ,  $\text{Au}_2\text{O}_3$ , and  $\text{Au}_2\text{O}_4$  exist, redetermined the atomic weight of the element, measured the spark spectrum given by a neutral solution of gold chloride, and, partly in connection with his students, investigated the compounds of gold with the halogens and with sulphur.

In 1886 he became Privatdocent at Munich, and in the following winter, 1886–7, he visited Nilson in Stockholm, beginning, under the guidance of that eminent investigator, his study of the rare earths. The remarkable industry with which they prosecuted their mutual researches is evidenced by the number and importance of the contributions appearing under their names in the *Berichte* for 1887.

The wide reputation which Krüss had thus so early won attracted to Munich many enthusiastic workers in the domain of inorganic chemistry, and the obtaining of a place in his private laboratory was a privilege that was eagerly sought. Upon those

who had the good fortune to work under his immediate direction the attraction exerted by his ability and wide and accurate learning was quite equaled by the charming personality of the man. Quiet and unassuming in manner, and never prone to dogmatic direction of the work in hand, he yet gave to each piece of research a critical attention and kindly and suggestive criticism that was wonderfully helpful and inspiring. Although he could scarcely be called either a graceful or a fluent lecturer, he possessed to an unusual degree originality and clearness in exposition. In May, 1890, he was advanced to the professorship of analytical and special inorganic chemistry in the University of Munich, and this position he held at the time of his death.

The latter part of Krüss's work lay chiefly in the obscure and difficult field of the rare earths, and while these researches are too numerous to admit of detailed mention here, a glance at the mere titles will suffice to show their variety and extent. Besides critically studying the characteristics of many of the different "earths," he greatly developed the methods of separation and examination of these allied elements. Among the many other admirable papers which appeared in the meantime there may be mentioned that with Moraht upon glucinum, with Ohnmais upon the sulpho-salts of vanadium, and with Thiele upon the condition of iodine in solution and the probable cause of the differences in color of its solutions.

The services of Professor Krüss to inorganic chemistry were still further increased by his founding in 1892 the *Zeitschrift für anorganische Chemie*, a journal which he edited with great skill and success. It met with very favorable reception from the beginning, and in the short space of three years it has fully attained what Krüss stated in his introduction to the first volume to be its goal—"to materially advance the development of inorganic chemistry."

The illness to which Krüss finally succumbed began as far back as last October, but in spite of bodily suffering he resolutely continued his lectures and instruction at the laboratory. With the new year, however, his strength began to fail and, gradually sinking, he finally passed away early on the morning of the third of February.

To those who knew Krüss and his work there will recur, as

aptly characterizing him, the words of Berzelius about Liebig—  
 "The man unites, to an unusual degree, unassuming amiability  
 with extraordinary industry and rare scientific ability."

L. M. DENNIS.

PUBLISHED RESEARCHES OF PROFESSOR KRÜSS.

- 1882. Ueber die Constitution von Lösungen, Ber. d. chem. Ges., 15, 1243.
- 1883. Ueber die Schwefelverbindungen des Molybdäns, Ber. d. chem. Ges., 16, 2044.
- 1883. With S. Oeconomides: Beziehungen zwischen der Zusammensetzung und den Absorptionsspektren organischer Verbindungen, Ber. d. chem. Ges., 16, 2051.
- 1883. Ueber die Schwefelverbindungen des Molybdäns, Ann. Chem. (Liebig), 225, 1.
- 1884. Ueber eine neue Darstellungsmethode für Nitrile, Ber. d. chem. Ges., 17, 1766.
- 1884. Ueber die Schwefelverbindungen des Molybdäns, Ber. d. chem. Ges., 17, 1769.
- 1884. Einige Beobachtungen über die höheren Sauerstoffverbindungen des Kupfers, Ber. d. chem. Ges., 17, 2593.
- 1884. Ueber den Einfluss der Temperatur auf spektralanalytische Beobachtungen und Messungen, Ber. d. chem. Ges., 17, 2732.
- 1885. Zur quantitativen Spectralanalyse, Ber. d. chem. Ges., 18, 983.
- 1885. Beziehungen zwischen der Zusammensetzung und den Absorptionsspektren organischer Verbindungen, Ber. d. chem. Ges., 18, 1426.
- 1885. Titerstellung der Lösungen von Kaliumpermanganat, Ber. d. chem. Ges., 18, 1580.
- 1885. Ueber innere Molekularbewegung, Ber. d. chem. Ges., 18, 2586.
- 1886. Ueber die Oxyde des Goldes, Ber. d. chem. Ges., 19, 2541.
- 1886. Ueber die Reducirbarkeit der anorganischen Sulfosalze durch Wasserstoff, Ber. d. chem. Ges., 19, 2729.
- 1886. Ueber einen Universalspectralapparat für qualitative und quantitative chemische Analyse, Ber. d. chem. Ges., 19, 2739.
- 1886. Untersuchungen über das Gold, (First Paper) Ann. Chem. (Liebig), 237, 274.
- 1887. Ueber das Atomgewicht des Goldes, Ber. d. chem. Ges., 20, 205.
- 1887. Ueber sublimirtes Aurichlorid, Ber. d. chem. Ges., 20, 211.
- 1887. Untersuchungen über das Gold, (Second Paper) Ann. Chem. (Liebig), 238, 30 and 241.
- 1887. With L. F. Nilson: Ueber das Aequivalent und Atomgewicht des Thoriums, Ber. d. chem. Ges., 20, 1665.
- 1887. With L. F. Nilson: Ueber die Erden und die Niobsäure des Fergusonites, Ber. d. chem. Ges., 20, 1676.
- 1887. With L. F. Nilson: Ueber das Product der Reduction von Niobfluorkalium mit Natrium, Ber. d. chem. Ges., 20, 1691.
- 1887. With L. F. Nilson: Ueber Kaliumgermanfluorid, Ber. d. chem. Ges., 20, 1696.

1887. With L. F. Nilson: Studien über die Componenten der Absorptionsspectra erzeugenden seltenen Erden, Ber. d. chem. Ges., 20, 2134.

1887. Ueber das Atomgewicht des Goldes, Ber. d. chem. Ges., 20, 2365.

1887. With Ludwig Hoffmann: Ueber die Sulfide des Goldes, (First Paper), Ber. d. chem. Ges., 20, 2369.

1887. With F. W. Schmidt: Beiträge zur Kenntniss der Goldhalogenverbindungen, Ber. d. chem. Ges., 20, 2634.

1887. With Ludwig Hoffmann: Ueber die Sulfide des Goldes (Second Paper), Ber. d. chem. Ges., 20, 2704.

1887. With L. F. Nilson: Die Componenten der Absorptionsspectra erzeugenden seltenen Erden, Ber. d. chem. Ges., 20, 3067.

1887. With L. F. Nilson: Ueber die Dampfdichte des Thoriumchlorids, Ztschr. phys. Chem., 1, 301.

1887. With L. F. Nilson: Ueber die spezifische Wärme des Niobwasserstoffs und der Niobsäure, Ztschr. phys. Chem., 1, 391.

1888. Ueber das Atomgewicht des Goldes, Ber. d. chem. Ges., 21, 126.

1888. Ueber ein neues Vorkommen des Germaniums, Ber. d. chem. Ges., 21, 131.

1888. With L. F. Nilson: Die Componenten der Absorptionsspectra erzeugenden seltenen Erden, Ber. d. chem. Ges., 21, 585.

1888. Beziehungen zwischen Zusammensetzung und Absorptionsspectrum organischer Verbindungen, Ztschr. phys. Chem., 2, 312.

1888. With Paul Kiesewetter: Beiträge zur Kenntniss der Absorptionsspectra erzeugenden seltenen Erden, Ber. d. chem. Ges., 21, 2310.

1888. With Erich Jäger: Zur volumetrischen Bestimmung der Kohlensäure in Carbonaten, Ztschr. anal. Chem., 27, 721.

1888. With F. W. Schmidt: Beiträge zur Kenntniss der Goldhalogenverbindungen, J. prakt. Chem., 38, 77.

1889. With F. W. Schmidt: Untersuchung über das Kobalt und Nickel, Ber. d. chem. Ges., 22, 11.

1889. With F. W. Schmidt: Untersuchung über Kobalt und Nickel, Notiz. Ber. d. chem. Ges., 22, 2026.

1889. With Erich Jäger: Untersuchung über das Chrom, Ber. d. chem. Ges., 22, 2028.

1889. With Hermann Moraht: Zur spectrocolumetrischen Eisen- bezw. Rhodan-Bestimmung, Ber. d. chem. Ges., 22, 2054.

1889. With Hermann Moraht: Ueber Eisendoppelrhodanide, Ber. d. chem. Ges., 22, 2061.

1889. With Max Althausse: Beziehungen zwischen Zusammensetzung und Absorptionsspectrum organischer Verbindungen, Ber. d. chem. Ges., 22, 2065.

1890. With Hermann Moraht: Untersuchungen über das Beryllium, Ber. d. chem. Ges., 23, 727 and 2552.

1890. With Karl Ohnmais: Ueber Vanadinsulfosalze, Ber. d. chem. Ges., 23, 2547.

1890. With Hermann Moraht: Untersuchung über das Beryllium (First Paper), Ann. Chem. (Liebig), 260, 161.

1890. With Hermann Morah: Ueber die Reaction zwischen Ferrisalzen und löslichen Rhodaniden, *Ann. Chem. (Liebig)*, **260**, 193.

1890. With Hermann Morah: Untersuchung über das Beryllium (Second Paper), *Ann. Chem. (Liebig)*, **262**, 38.

1890. With Karl Ohnmais: Ueber Sulfosalze des Vanadins, *Ann. Chem. (Liebig)*, **263**, 39.

1891. Beiträge zur Chemie des Erbiums und Didyms, *Ann. Chem. (Liebig)*, **265**, 1.

1892. With H. Krüss: Beiträge zur quantitativen Spektralanalyse, *Ztschr. anorg. Chem.*, **1**, 104.

1892. With Hermann Morah: Ueber die Reaktion zwischen Ferrisalzen und löslichen Rhodaniden, *Ztschr. anorg. Chem.*, **1**, 399.

1892. With F. W. Schmidt: Atomgewichtsbestimmungen von Nickel, *Ztschr. anorg. Chem.*, **2**, 235.

1892. Einige Bemerkungen über die Untersuchung der seltenen Gadoliniterden, im besonderen über die Aequivalentbestimmung dieser Erden durch Ueberführung von Oxyd in Sulfat, *Ztschr. anorg. Chem.*, **3**, 44.

1892. Elektrolyse von Lösungen seltener Erden, *Ztschr. anorg. Chem.*, **3**, 60.

1893. With K. Hofmann: Einwirkung von Kohle auf Salzlösungen seltener Erden, *Ztschr. anorg. Chem.*, **3**, 89.

1893. With A. Loose: Verhalten der Gadoliniterden gegen Kaliumchromat, *Ztschr. anorg. Chem.*, **3**, 92.

1893. Verhalten der Gadoliniterden gegen Anilin und gegen salzsaures Anilin, *Ztschr. anorg. Chem.*, **3**, 108.

1893. Ueber die Bildung von Sulfosalzen des Vanadins, *Ztschr. anorg. Chem.*, **3**, 264.

1893. Ueber die Erbinerde, *Ztschr. anorg. Chem.*, **3**, 353.

1893. With F. W. Schmidt: Ueber die Doppelhalogenverbindungen des Goldes, *J. prakt. Chem.*, **47**, 301.

1893. With K. Hofmann: Ueber die Holminerde, *Ztschr. anorg. Chem.*, **3**, 407.

1893. With F. W. Schmidt: Ueber die Einwirkung von Chlor und Brom auf Gold, *Ztschr. anorg. Chem.*, **3**, 421.

1893. With K. Hofmann: Ueber die Terbinerde, *Ztschr. anorg. Chem.*, **4**, 27.

1893. With Anton Loose: Annähernde Bestimmung des Aequivalents seltener Erden durch Titration, *Ztschr. anorg. Chem.*, **4**, 161.

1893. With Conrad Volk: Zur Kenntniss der Schwefelverbindungen des Thoriums, *Ztschr. anorg. Chem.*, **5**, 75.

1894. Zur Kenntniss der Schwefelverbindungen des Thoriums, *Ztschr. anorg. Chem.*, **6**, 49.

1894. With Edmund Thiele: Ueber den Lösungszustand des Iod und die wahrscheinliche Ursache der Farbenunterschiede seiner Lösungen, *Ztschr. anorg. Chem.*, **7**, 52.

---



## THE PROTEIDS OF THE RYE KERNEL.<sup>1</sup>

By THOMAS B. OSBORNE.

Received April 8, 1895.

THE proteids of this seed have been but little studied and the statements published leave the subject in much confusion.

Einhof, who in 1805<sup>2</sup> undertook an analysis of rye, was the first to make observations on the proteids obtained therefrom. He found that an aqueous extract of rye-meal contained two distinct proteid substances, one coagulating on boiling, and insoluble in alcohol, which he called albumin, and the other not coagulating, but soluble in alcohol, which he called gluten [kleber]. The latter he considered to be identical with the similar substance extracted from wheat gluten by alcohol. Treatment with alcohol yielded much more "kleber" than was extracted by water alone. It is interesting to note that Einhof in this investigation first discovered that characteristic differences exist between different kinds of vegetable proteid matter, it being thought at that time that gluten and albumin were simply modifications of the same body which under like conditions would show the same properties.

Heldt<sup>3</sup> in 1843 published a description of the proteid taken up by alcohol from rye-meal. He prepared it by extracting the meal with hot alcohol, distilling off the alcohol, and treating the residue with ether to remove fat, and with water to remove ether and sugar.

This preparation was analyzed with the following result:

Carbon .....	56.38
Hydrogen .....	7.87
Nitrogen .....	15.83
Sulphur } .....	19.92
Oxygen } .....	

---

100.00

<sup>1</sup> From the report of the Connecticut Agricultural Experiment Station for 1894. Communicated by the author.

<sup>2</sup> *J. d. Chem. v. Gehlen*, 5, 131.

<sup>3</sup> *Ann. d. Chem. u. Pharm.*, 45, 195.

Heldt remarked, "the same composition was found by Scherer and Jones for other nitrogenous constituents of plants, plant-casein, plant-albumin, and plant-gelatin, to which last this body appears to stand nearest."

Jones<sup>1</sup> obtained albumin from rye by boiling the aqueous extract and treating the resulting coagulum with ether. He states that this albumin contained :

Carbon .....	54.74
Hydrogen.....	7.77
Nitrogen .....	15.85
Oxygen .....	21.64
	<hr/>
	100.00

Verdeil,<sup>2</sup> contrary to the experience of Einhof, von Bibra, Ritthausen, and the writer, obtained gluten from rye-meal by kneading and washing in a cloth until starch was removed. He states that there remained a tough, glutinous substance, which could be easily drawn into threads. This gluten he says was not pure but was contaminated with a substance soluble in alcohol. When thoroughly extracted with alcohol he considered it to be pure. He determined sulphur in the gluten and found 0.989 and 0.972 per cent. Von Bibra<sup>3</sup> considered the proteid extracted from rye by alcohol to be the same as that similarly obtained from wheat. He gave the nitrogen content of this body as 15.73, 15.52, and 15.50, and the sulphur as 0.973 and 0.950 per cent. He also recognized the presence of "casein" which he did not analyze, and found from 1.565 to 2.799 per cent. of albumin, which contained 15.53 and 15.42 per cent. of nitrogen. He considered the proteids of rye to be the same as those of wheat.

Rittenhausen<sup>4</sup> described three proteid substances which he found in rye; albumin, soluble in water, mucedin, soluble in alcohol, and gluten-casein, soluble in dilute potash water but insoluble in water and cold alcohol.

Albumin, he says, is present in the aqueous extracts but he made no further examination of this body. The mucedin he considers to be the only proteid, soluble in alcohol, present in

<sup>1</sup> *Ann. d. Chem. u. Pharm.*, 40, 66.

<sup>2</sup> *Ann. d. Chem. u. Pharm.*, 58, 319.

<sup>3</sup> *Die Getreidearten u. das Brod*, Nuernberg, 1860, 291.

<sup>4</sup> *J. prakt. Chem.*, 99, 439, and *Die Eiweisskoerper*, etc., Bonn. 1872, p. 83.

the rye kernel and this he regarded as similar to the mucedin which was believed to exist in the wheat kernel. He was unable to detect the presence of gliadin. Mucedin was prepared by extracting the meal with hot alcohol of eighty-five per cent. and concentrating and cooling the solution. The deposited substance was further extracted with alcohol and ether. It was then dissolved in acetic acid and fractionally precipitated with potash. He states the composition of the substance as :

Carbon .....	53.61
Hydrogen .....	6.79
Nitrogen .....	16.84
Sulphur .....	0.50
Oxygen .....	22.26
	<hr/>
	100.00

The gluten-casein was obtained by extracting the rye-meal directly with very dilute potash-water, precipitating with acetic acid and washing with water, alcohol, and ether. Two preparations were made and gave, as an average, the following figures on analysis :

Carbon.....	52.14
Hydrogen .....	6.93
Nitrogen .....	16.38
Sulphur.....	1.06
Oxygen .....	23.49
	<hr/>
	100.00

Sidney Martin<sup>1</sup> states that wheat, rye, and barley contain a globulin substance similar in properties to animal myosin, being soluble in ten to fifteen per cent. sodium chloride solutions, precipitated therefrom by saturation with sodium chloride and with magnesium sulphate, and coagulating at 55° to 60°. This globulin is precipitated by dialysis and thereby is converted into the albuminate form. It is very evident from the foregoing summary of previous work that we have no satisfactory knowledge of the rye proteids.

In presenting the results of my investigation the subject may be most conveniently discussed under the following heads :

A, proteids soluble in water ; B, proteids insoluble in water

<sup>1</sup>*Jour. Physiol.*, 8, viii.

but soluble in saline solutions; C, proteids insoluble in water and in saline solutions but soluble in alcohol; and, D, proteids insoluble in water, saline solutions, or alcohol but soluble in dilute alkalies.

A. PROTEIDS SOLUBLE IN WATER. LEUCOSIN. PROTEOSE.

The proteids soluble in water are best examined in extracts made in the first instance with ten per cent. sodium chloride solution from which subsequently the soluble salts have been removed by prolonged dialysis. When water is applied to the grain it becomes a weak saline solution which not only takes up globulins but also extracts gliadin whose presence greatly complicates the examination of the water-soluble proteids. Rye-meal<sup>1</sup> was accordingly exhausted with a solution containing ten per cent. sodium chloride and the extract, after syphoning from the subsided insoluble matters, was freed from salts and globulin by dialysis in river water and filtration. The resulting solution yielded no more globulin by dialysis in distilled water and contained only those proteids extracted from the seed which were soluble in pure water. As the extract was bulky the proteids were precipitated by saturation with ammonium sulphate and thereupon dissolved in water. A comparatively concentrated solution was thus obtained which was very nearly freed from ammonium sulphate by dialysis. It then had the following properties: When heated slowly it became turbid at 52° and particulate at 63°. After filtering from this coagulum nothing more separated even on boiling. Saturation of the dialyzed solution with sodium chloride gave a precipitate that dissolved readily in water to a solution, which, heated to 63°, yielded a coagulum of albumin. The filtrate from this coagulum was again saturated with salt and a considerable precipitate obtained showing that with the albumin some proteose-like body was thrown down. Nitric acid added to the solution of this precipitate in water gave a precipitate which dissolved on warming and reappeared on cooling. The solution after filtering out the first precipitate of proteose and albumin, produced by saturation with sodium chloride, gave more precipitate on adding acetic

<sup>1</sup> The rye-meal used throughout this work was obtained by grinding, in the laboratory, portions of clean and fresh winter rye, as needed for each extraction.

acid, showing the presence of a further quantity of proteose. The coagulum above described, which separated on heating its solution to 65°, was washed thoroughly with water, alcohol, absolute alcohol, and ether, and dried over sulphuric acid. When dried at 110° it had the following composition :

COAGULATED RYE ALBUMIN, LEUCOSIN, *Preparation 1.*

	I.	II.	Average.	Ash-free.
Carbon.....	52.31	....	52.31	52.57
Hydrogen .....	6.78	....	6.78	6.81
Nitrogen .....	16.14	16.11	16.13	16.22
Sulphur } .....	....	....	....	24.40
Oxygen }	....	....	....	100.00
Ash .....	0.51			

Another extract was examined in a slightly different way. 1,000 grams of rye-meal were extracted with eleven liters of ten per cent. sodium chloride solution and, in order to get rid of the large amount of gum taken up, the solution, after filtering, was dialyzed and then saturated with ammonium sulphate. The precipitate thus produced was dissolved, as far as possible, in ten per cent. sodium chloride brine, filtered clear, and dialyzed until chlorides were removed. The solution after filtering clear was then heated to 65° and the albumin that separated was filtered out, washed thoroughly with hot water, with alcohol, and with ether, and dried over sulphuric acid. This preparation, 2, weighed 1.21 grams and had the following composition :

COAGULATED RYE ALBUMIN, LEUCOSIN, *Preparation 2.*

		Ash-free.
Carbon .....	53.04	53.29
Hydrogen .....	6.70	6.74
Nitrogen .....	16.57	16.65
Sulphur } .....	....	23.32
Oxygen }	....	100.00
Ash.....	0.50	

The solution containing the proteoses, filtered from preparation 2, was then treated with twenty per cent. of its weight of dry sodium chloride and a little two-tenths per cent. hydrochloric acid was added which gave a considerable precipitate.

This was filtered out, dissolved in distilled water, and the solution dialyzed till free from chlorides. This solution then gave a precipitate with nitric acid, which dissolved on warming and precipitated again on cooling. The solution concentrated to a syrup on a water-bath was precipitated by pouring into absolute alcohol. The precipitate, when dried over sulphuric acid, weighed 0.41 gram or one-third as much as the albumin. The filtrate, from the precipitation of this substance [with twenty per cent. of sodium chloride and acid], was saturated with ammonium sulphate and the precipitate thus produced filtered out and dissolved in distilled water. With copper sulphate and potash this substance gave a clear pink color. Its solution gave no precipitate on adding nitric acid until it had been saturated with sodium chloride, when a slight precipitate fell. It yielded no precipitate with copper sulphate. These reactions indicate that besides albumin the aqueous extract contains small quantities of proto- and deuterio-proteose.

Again, 2,000 grams of rye-meal were treated with ten per cent. sodium chloride solution and the extract filtered and saturated with ammonium sulphate. The precipitate produced was dissolved in ten per cent. sodium chloride solution, filtered, and dialyzed until all chlorides were removed. After filtering clear the solution was heated to 65° for some time and the coagulum filtered out, washed with hot water, alcohol, and ether, and dried for analysis, preparation 3. The filtrate from 3 was then concentrated by boiling, during which a coagulum developed. This was filtered out, washed as usual, and dried for analysis, preparation 4.

COAGULATED RYE ALBUMIN, LEUCOSIN, *Preparation 3.*

	I.	II.	Average.	Ash-free.
Carbon.....	53.41	53.32	53.37	53.52
Hydrogen .....	6.90	6.82	6.86	6.88
Nitrogen.....	16.73	....	16.73	16.78
Sulphur } .....	....	....	....	22.82
Oxygen }				
				<hr/> 100.00
Ash.....	0.30			

COAGULATED RYE ALBUMIN, LEUCOSIN, *Preparation 4.*

	I.	II.	Average.	Ash-free.
Carbon.....	52.64	52.53	52.58	52.86
Hydrogen .....	6.76	6.73	6.75	6.79
Nitrogen .....	16.86	....	16.86	16.95
Sulphur } .....	....	....	....	23.40
Oxygen }				
				<hr/> 100.00
Ash.....	0.56			

Another extract was made by treating 1,700 grams of rye-meal with sixteen liters of water. After standing over night the solution was filtered off and saturated with ammonium sulphate. The meal residue was treated again in the same way and the filtered extract, after saturating with ammonium sulphate, was added to that first obtained. The precipitated proteids were then dissolved in water yielding a very gummy solution. As this solution was bulky the proteids were again precipitated with ammonium sulphate and the precipitate after filtering out was treated with three liters of ten per cent. sodium chloride solution. The whole was then dialyzed, it having been found that these viscid solutions lost their gummy character on dialysis. After eight days all the gum had disappeared. The solution was then readily filtered clear. In order to reduce the volume of the solution it was again saturated with ammonium sulphate and the large precipitate treated with about a liter of ten per cent. sodium chloride solution. A turbid liquid resulted which was not cleared by passing through filter-paper but, on standing, became clear and the sediment was found to consist of gliadin, which is to be noticed later. Gliadin is soluble to a considerable extent in pure water and in water containing but a very small amount of dissolved salts, but the addition of a little sodium chloride to its solution precipitates it completely. After the solution had entirely cleared by subsidence it was dialyzed free from chlorides and heated to 65°. The resulting coagulum was then filtered out, washed and dried in the usual manner, and found to weigh 1.55 grams. The composition of this preparation was as follows:

[illegible]



Five hundred grams of rye flour<sup>1</sup> were extracted with 2,000 cc. of five per cent. sodium chloride solution and 1,000 cc. of the clear filtered extract were dialyzed till free from chlorides. The solution was then filtered and heated for twenty-four hours in a water-bath of 70°. The coagulated albumin was filtered out, washed with water, alcohol, and ether, and dried over sulphuric acid, and found to weigh 1.08 grams, equivalent to 0.43 per cent. of the flour.

So far as tested this albumin agrees in all respects with that obtained from wheat.<sup>2</sup> The variations in composition of these preparations are considerable but perhaps not greater than might be expected.

The aqueous and saline extracts of the rye-meal contain much gum and coloring matters which render the isolation of pure proteids very difficult. It will be seen, however, that the preparations of wheat albumin and rye albumin have very nearly the same average composition and that both proteids show the same reactions and coagulate at the same temperature. They are unquestionably the same substance, for which I have adopted the name *leucosin*.

## COAGULATED LEUCOSIN.

	Wheat. Average of five analyses.	Rye. Average of six analyses.
Carbon .....	53.02	52.97
Hydrogen .....	6.84	6.79
Nitrogen .....	16.80	16.66
Sulphur .....	1.28	1.35
Oxygen .....	22.06	22.23
	<hr/> 100.00	<hr/> 100.00

The proteoses of the rye also show the same reactions as those of the wheat kernel, and so far as it is possible to determine they are identical.

## B. PROTEID SOLUBLE IN SALINE SOLUTIONS. EDESTIN.

Owing to the large amount of gum extracted from the rye-meal, the preparation of the globulin in a pure state was found to be extremely difficult. Such preparations as were made disagreed

<sup>1</sup> Made by the Health Food Company of New York.

<sup>2</sup> *Am. Chem. J.*, 15, 408; also Ann. Report Conn. Expt. Station for 1893, p. 179.

in composition and in only one case was a substance obtained which appeared to be pure enough to warrant the publication of its analysis. So far as could be detected the globulin which separated on dialysis had the same properties as that similarly derived from wheat. One preparation of this globulin, which had nearly the same composition as the wheat globulin and appeared to be free from gum and other impurities, was obtained as follows: 5,000 grams of rye flour, made by the Health Food Co. of New York, were extracted with fifteen liters of five per cent. sodium chloride solution and the extract filtered clear. Nine liters of extract were thus obtained, being approximately equal to a complete extraction of three kilos of rye flour.

The entire solution was dialyzed for four days in order to remove the greater part of the gum. The extract was saturated with ammonium sulphate, the precipitate filtered out, suspended in water, and dialyzed for three days. Most of the substance was now dissolved and the insoluble matter was filtered out, washed with sodium chloride solution, and the filtrate and washings returned to the dialyzer. When free from chlorides the solution was filtered from a small precipitate and this latter washed with water, alcohol, and ether and dried over sulphuric acid. Only 1.21 grams of globulin were obtained, which, when dried at 110°, had the following composition:

RYE GLOBULIN, EDESTIN, *Preparation 7*. WHEAT GLOBULIN, EDESTIN.

		Ash-free.	Average of five analyses.
Carbon.....	51.03	51.19	51.03
Hydrogen .....	6.72	6.74	6.85
Nitrogen.....	18.14	18.19	18.39
Sulphur } .....		23.88	0.69
Oxygen } .....			23.04
Ash.....	0.33	100.00	100.00

The writer has no doubt that this globulin is identical with the *edestin* found in the wheat kernel and other seeds,<sup>1</sup> but owing to the difficulties encountered in preparing it from rye, further evidence on this point was not obtained.

With reference to Martin's statement concerning the presence of myosin—what is written on that point in the paper by Osborne

<sup>1</sup> Annual Report Conn. Expt. Station for 1893, pp. 179 and 216.

and Voorhees on the "Proteids of the Wheat Kernel" applies equally to rye.<sup>1</sup>

### C. PROTEID SOLUBLE IN ALCOHOL. GLIADIN.

After extraction with sodium chloride solution, alcohol of seventy-five to eighty per cent. takes up a considerable quantity of proteid. One hundred grams of rye-meal were extracted thoroughly with ten per cent. sodium chloride solution and then with seventy-five per cent. alcohol. The alcoholic extract was evaporated to very small volume and the separated proteid washed with water and ether and then dried. It weighed 3.93 grams, being therefore nearly four per cent. of the meal. Two thousand grams of rye-meal were then extracted with alcohol of 0.9 specific gravity, four successive times. Each extract, after filtering clear, was concentrated by distillation on a water-bath. The first three extracts yielded, on cooling, a deposit of proteid, but the fourth contained almost none. Each residue was then washed with water and dissolved in seventy-five per cent. alcohol. The substance from the first extract yielded an insoluble residue which, when washed with dilute alcohol, absolute alcohol, and ether, gave preparation 8. This dried at 110° contained seventeen per cent. of nitrogen. The solutions of the substances from the three extracts in dilute alcohol, were concentrated to about one-fourth their original volume and cooled, when the dissolved proteid separated. The substance from the first extract was digested with absolute alcohol which dissolved a part of it, then with ether, and dried, giving preparation 9. The residue from the second extract was washed superficially with water and then treated in a divided state with distilled water until dissolved. A little saturated sodium chloride was then added and the proteid wholly precipitated. The precipitate was then thoroughly dehydrated with absolute alcohol, digested with ether, and dried. This formed preparation 10. The proteid separated from the third extract was digested with absolute alcohol and with ether, and yielded a small quantity of proteid, preparation 11, which when dried contained, ash-free, 16.89 per cent. of nitrogen. The absolute alcohol used in dehydrating preparation 9, with help of the water which it extracted, dissolved a con-

<sup>1</sup> *Am. Chem. J.*, 18, 415.

siderable quantity of proteid. This was precipitated by adding a few drops of sodium chloride solution. The precipitate produced was then digested with absolute alcohol and ether and, when dried was found to contain, ash-free, 16.02 per cent. of nitrogen. The preparation was therefore redissolved in dilute alcohol, filtered perfectly clear, concentrated to small volume, and cooled. The proteid separating was then treated as before with absolute alcohol and ether and yielded preparation 12. The proteid thus extracted showed in all respects the properties of wheat gliadin, and it will be seen that it has nearly the same composition.

RYE GLIADIN, *Preparation 9.*

	I.	II.	Average.	Ash-free.
Carbon .....	52.76	....	52.76	52.84
Hydrogen .....	6.81	....	6.81	6.82
Nitrogen.....	17.14	17.23	17.19	17.22
Sulphur } .....	....	....	....	23.12
Oxygen } .....	....	....	....	23.12
Ash .....	0.16			100.00

RYE GLIADIN, *Preparation 10.*

	I.	II.	Average.	Ash-free.
Carbon .....	53.06	52.90	52.98	53.23
Hydrogen .....	6.83	7.11	6.97	7.00
Nitrogen .....	17.13	17.17	17.15	17.23
Sulphur } .....	....	....	....	22.54
Oxygen } .....	....	....	....	22.54
Ash .....	0.48			100.00

RYE GLIADIN, *Preparation 12.*

	I.	II.	Average.	Ash-free.
Carbon.....	52.99	53.11	53.05	53.11
Hydrogen.....	6.73	6.83	6.78	6.79
Nitrogen .....	17.57	....	17.57	17.59
Sulphur .....	1.44	....	1.44	1.44
Oxygen .....	....	....	....	21.07
Ash .....	0.12			100.00

One thousand grams of rye-meal were thoroughly extracted with ten per cent. sodium chloride solution and drained as dry as possible on filters. The extracted residue was then treated with alcohol of 0.860 specific gravity four consecutive times. The four red-brown extracts were filtered clear, concentrated till most

of the alcohol was removed, and then cooled. The precipitates thus obtained were united and treated at first with stronger and afterwards with seventy-five per cent. alcohol until all soluble was dissolved. A considerable residue remained which appeared to be coagulated gliadin. This was washed thoroughly with absolute alcohol and ether, and when dried weighed 5.62 grams, preparation 13. The dissolved proteid, after filtering its solution perfectly clear, was separated by concentrating to small volume and cooling. The deposit was then treated with absolute alcohol, dissolved again in a little dilute alcohol, and precipitated by pouring into absolute alcohol. The proteid, preparation 14, separated perfectly colorless, in a finely divided state. When dried it weighed 11.66 grams.

*RYE GLIADIN, Preparation 13.*

	I.	II.	Average.	Ash-free.
Carbon.....	52.36	....	52.36	52.62
Hydrogen .....	6.73	....	6.73	6.76
Nitrogen .....	17.75	17.59	17.67	17.75
Sulphur.....	1.19	....	1.19	1.19
Oxygen .....	....	....	....	21.68
				<hr/> 100.00
Ash .....	0.51			

*RYE GLIADIN, Preparation 14.*

	I.	II.	Average.	Ash-free.
Carbon.....	52.74	....	52.74	52.93
Hydrogen .....	6.73	....	6.73	6.75
Nitrogen .....	17.32	17.52	17.42	17.48
Sulphur.....	1.23	....	1.23	1.23
Oxygen .....	....	....	....	21.61
				<hr/> 100.00
Ash .....	0.37			

These two preparations formed together 1.73 per cent. of the rye-meal and have the composition of wheat gliadin. In order to prevent contamination of this proteid with the gum contained in rye-meal, which Ritthausen<sup>1</sup> states to be freely soluble in fifty per cent. alcohol, the following method was tried:

After extracting rye-meal with ten per cent. sodium chloride

<sup>1</sup> Die Eiweisskoerper, etc., Bonn, 1872, p. 96, and *J. prakt. Chem.*, 99, 454, and 102, 321.

brine, the residue was treated with alcohol so strong that with the water retained by the meal, a mixture resulted containing about seventy-five per cent. of alcohol. After standing over night the extract was syphoned from the residue and greatly diluted with water. The proteid separated on standing and was filtered out and dissolved in seventy-five per cent. alcohol. This solution was filtered perfectly clear, concentrated, cooled, and the separated proteid treated with absolute alcohol and ether and dried. The resulting preparation 15, was perfectly white. The residual meal was again extracted with seventy-five per cent. alcohol and the extract filtered clear, concentrated to one-fourth its volume, cooled, the precipitated proteid again dissolved in seventy-five per cent. alcohol, filtered clear, concentrated, cooled, and the separated proteid washed repeatedly with water. The substance was again dissolved in dilute alcohol and the clear solution precipitated by pouring into absolute alcohol. The precipitate produced was still again dissolved in dilute alcohol and a second time precipitated by pouring into absolute alcohol. The precipitate thus resulting was dissolved in dilute alcohol and precipitated by pouring into water and adding a little salt. The final pure white precipitate was digested with absolute alcohol and ether and dried, giving preparation 16.

RYE GLIADIN, *Preparation 15.*

	I.	II.	Average.	Ash-free.
Carbon.....	52.03	52.09	52.06	52.40
Hydrogen.....	6.78	6.91	6.85	6.89
Nitrogen.....	17.80	....	17.80	17.91
Sulphur.....	1.23	....	1.23	1.24
Oxygen .....	....	....	....	21.56
				100.00
Ash .....	0.68			

RYE GLIADIN, *Preparation 16.*

	I.	II.	Average.	Ash-free.
Carbon.....	52.74	52.65	52.70	53.03
Hydrogen.....	6.90	6.96	6.93	6.97
Nitrogen.....	17.39	....	17.39	17.50
Sulphur.....	1.29	....	1.29	1.30
Oxygen .....	..	....	....	21.20
				100.00
Ash .....	0.65			

Another preparation of this substance was made by extracting three thousand grams of rye flour directly with seventy-five per cent. alcohol. The extract was concentrated to one-fourth its volume and the proteid which separated on cooling was washed many times with distilled water and dissolved in dilute alcohol, yielding a clear solution. This was then poured into three times its volume of absolute alcohol and an opalescent mixture obtained which deposited a curdy precipitate after adding a little sodium chloride solution. The strong alcoholic solution from which this separated was clear and of a deep yellow color. The precipitate was treated with absolute alcohol as long as this was colored. During the process the substance was rubbed up to a fine powder. It was finally digested with ether for twenty-four hours and dried over sulphuric acid. This preparation, 17, weighed fifty-eight grams, and was perfectly white. It formed very nearly two per cent. of the meal.

*RYE GLIADIN, Preparation 17.*

Carbon.....	52.68
Hydrogen .....	6.71
Nitrogen .....	17.89
Sulphur.....	1.22
Oxygen .....	21.50
Ash.....	0.00
	<hr/>
	100.00

In order to establish conclusively whether more than one alcohol-soluble proteid is contained in the rye kernel, five preparations were made from the same portion of meal, by fractional precipitation. Four thousand grams of rye-meal were thoroughly extracted with ten per cent. sodium chloride solution, and the greater part of the bran removed by washing the meal through coarse cloth with the salt solution. The residue, after decanting the salt solution was extracted with seventy-five per cent. alcohol; the extract was filtered clear and divided into two parts. The first part was concentrated to one-fourth and cooled, the second to one-half. The precipitated proteid from each was washed repeatedly with distilled water, dissolved in a small amount of seventy-five per cent. alcohol, filtered clear, and pre-

cipitated by pouring into absolute alcohol. The proteid thus separated was digested with absolute alcohol and with ether. From the first portion of the alcoholic extract, preparation 18 was obtained, from the second, preparation 19. These had the following composition :

RYE GLIADIN, *Preparation 18.*

		Ash-free.
Carbon.....	51.90	52.67
Hydrogen .....	6.87	6.97
Nitrogen .....	17.50	17.76
Sulphur .....	1.26	1.27
Oxygen .....	....	21.33
		<hr/>
		100.00
Ash .....	1.48	

RYE GLIADIN, *Preparation 19.*

		Ash-free.
Carbon .....	52.04	52.40
Hydrogen .....	6.66	6.71
Nitrogen .....	17.77	17.89
Sulphur.....	1.15	1.16
Oxygen.....	....	21.84
		<hr/>
		100.00
Ash .....	0.71	

The water washings from these two preparations were severally mixed with a little saturated sodium chloride solution which gave a considerable precipitate in each. These precipitates were then washed superficially with distilled water, dehydrated with absolute alcohol, and treated with ether. The washings from 18 yielded preparation 20, those from 19, preparation 21.

RYE GLIADIN, *Preparation 20.*

	I.	II.	Average.	Ash-free.
Carbon .....	51.36	51.55	51.46	53.05
Hydrogen .....	7.07 <sup>1</sup>	6.61	6.61	6.92
Nitrogen.....	17.64	17.61	17.63	18.17
Sulphur .....	1.14	....	1.14	1.17
Oxygen .....	....	....	....	20.69
				<hr/>
				100.00
Ash .....	3.01			

<sup>1</sup> Omitted in average.



	I.	II.	Average.	Ash-free.
Carbon .....	52.01	....	52.01	52.37
Hydrogen.....	6.88	....	6.88	6.93
Nitrogen.....	17.99	17.97	17.98	18.10
Sulphur .....	1.04	....	1.04	1.05
Oxygen .....	....	....	....	21.55

		Ash-free.
Carbon .....	48.44	52.46
Hydrogen .....	6.22	6.73
Nitrogen .....	16.68	17.94
Sulphur .....	0.91	0.99
Oxygen .....	....	21.88

[illegible]

Comparing these results with those obtained by Osborne and Voorhees in analyzing gliadin from wheat<sup>1</sup> it is seen that they agree very closely, similar variations between the analyses existing in both cases. The averages of the two series of analyses agree well, as shown by the following figures :

GLIADIN.		
	Wheat.	Rye.
Carbon .....	52.72	52.75
Hydrogen .....	6.86	6.84
Nitrogen .....	17.66	17.72
Sulphur .....	1.14	1.21
Oxygen .....	21.62	21.48
	<hr/> 100.00	<hr/> 100.00

In all their properties wheat gliadin and rye gliadin resemble each other so exactly as to leave no doubt of their chemical identity. Ritthausen, as already stated, failed to find gliadin in rye-meal and described the proteid soluble in alcohol as mucedin, having a lower nitrogen and higher carbon content. This disagreement is doubtless due to impurities in Ritthausen's preparations, which, as he mentions, contained coloring matter that could not be removed. This color was probably a result of extracting with hot alcohol, which Ritthausen appears to have used in all cases, cold alcohol having given him a small yield of proteid. I had, however, no trouble in obtaining an abundant yield of gliadin with cold alcohol of seventy per cent., and thereby have extracted far less coloring matter than with hot alcohol.

#### D. PROTEID SOLUBLE ONLY IN DILUTE ALKALIES.

The sample of rye flour previously used in this work contained 1.52 per cent. of nitrogen. The amount of nitrogen soluble in salt solution and in dilute alcohol was determined in this flour by extracting 100 grams with a large quantity of five per cent. sodium chloride solution and then with seventy-five per cent. alcohol. The residue was then thoroughly air-dried and found to weigh seventy-eight grams. This residue contained 0.55 per cent. of nitrogen. The 100 grams of flour therefore con-

<sup>1</sup> *Am. Chem. J.*, 15, 436.

tained 1.52 grams of nitrogen of which 0.43 gram remained after extraction and 1.09 grams were soluble in dilute salt solution and alcohol, or in other words, 71.7 per cent. of the nitrogen was soluble in the reagents named and 28.3 per cent. was insoluble. In the wheat kernel a considerable part of the nitrogen was likewise found to be insoluble in salt solution and in dilute alcohol, but as this substance could be separated as a constituent of the gluten it was possible to prepare it in quantity and in a state of comparative purity. Since rye flour yielded no gluten on washing with water, the proteid remaining in the meal after extracting with salt solution and dilute alcohol, could be obtained only by extracting the residual meal directly with dilute potash water. All attempts, however, to thus prepare this substance resulted only in the production of small preparations of very variable composition. The gum present in the seed dissolved freely in the alkaline solution and made it impossible by any means yet discovered to thoroughly purify the preparations. For this reason nothing positive can be said now in relation to the nature or composition of this residual proteid. Since the other proteids are the same as those found in the wheat kernel it might be conjectured that this proteid is identical with glutenin. The fact that rye flour yields no gluten is, however, opposed to such a conclusion. It is therefore more probable that the substance in question is, partly or wholly, other than glutenin.

#### QUANTITIES OF THE DIFFERENT PROTEIDS IN THE RYE KERNEL.

Owing to the gum already mentioned the filtration and treatment of the rye extracts was difficult and prolonged and the amounts of globulin, albumin, and proteose could not be determined separately, as in the case of wheat. The rye flour contained 1.52 per cent. of nitrogen. If we assume that the proteids of rye contain on the average 17.6 per cent. of nitrogen, as was very nearly the case with those of wheat, and that all the nitrogen exists in proteid form, this sample of flour would contain 8.63 per cent. of proteid. We have, therefore, 2.44 per cent. of insoluble proteid and 6.19 per cent. soluble in salt solution and alcohol. We have already shown that the alcohol-soluble gliadin amounted to four per cent. of the flour and the

leucosin to 0.43 per cent.; there thus remains 1.76 per cent. to be divided between edestin and proteoses.

Insoluble in salt solution .....	2.44 per cent.
Gliadin, soluble in alcohol .....	4.00 "
Leucosin, soluble in water .....	0.43 "
Edestin and Proteose, soluble in salt solution	1.76 "
	<hr/>
	8.63 "

### ZIRCONIUM SULPHITE.

BY F. P. VENABLE AND CHARLES BASKERVILLE.

Received March 30, 1895.

VERY little is recorded in the text-books on chemistry with regard to this compound of zirconium. Berthier is reported as having examined it and found it to be a white insoluble body, slightly soluble, however, in an aqueous solution of sulphurous acid, from which it is thrown down again upon boiling. Whether this was what is commonly known as the neutral, or the acid, or a basic sulphite, is not recorded. It is highly probable that with so weak an acid as sulphurous acid, zirconium would form under these circumstances only basic compounds. We may state with regard to our own work that we have been unable with one exception to form any sulphite corresponding to the acid or the neutral. Only very indefinite compounds or mixtures of the sulphite with the hydroxide have come into our hands, as a rule.

The subject was first brought to our attention by the study of the reaction utilized by Baskerville for the quantitative separation of zirconium from iron and aluminum.<sup>1</sup> It was also put into use by him for shortening the method of preparing the pure zirconium chlorides.<sup>2</sup> The reaction in question is that which takes place when a nearly neutral solution of zirconium chloride is boiled with sulphur dioxide in excess.

Several points of interest were observed as to this reaction. It was found that when a solution of the sulphate was used it was difficult to secure any precipitation by means of sulphur dioxide even with persistent boiling. The chloride was clearly

<sup>1</sup> THIS JOURNAL, 16, 475.

<sup>2</sup> J. Elisha Mitchell, Scientific Society, 11, 85.

the best salt to use. The pure chloride was made up into approximately a two and a half per cent. solution and this was either very nearly neutralized by means of ammonia, or ammonia was added until there was a slight permanent precipitate. In the latter case the saturation of this solution with sulphur dioxide produced an immediate precipitate. If this were permitted to stand for some time the precipitate was redissolved, the remaining liquid being only slightly clouded. This re-solution was probably due to the hydrochloric acid liberated and also to the excess of sulphurous acid present. If this solution of zirconium chloride saturated with sulphur dioxide were diluted with several times its volume of water and boiled from fifteen to thirty minutes, a heavy white precipitate was produced. This was quite easily filtered by means of an unglazed porcelain suction filter. The precipitate was washed several times and finally dried over sulphuric acid in a desiccator. The analysis gave :

Zirconium dioxide.....	61.10	61.75	61.75	61.00	....	....
Sulphur dioxide.....	....	....	....	....	22.24	22.20
Ratio of zirconium to sulphur dioxide is 2 : 1, approximately.						
Ratio of zirconium to sulphur dioxide in the neutral sulphite, $Zr(SO_3)_2$ , is 1 : 1.4.						

This substance when so dried was perfectly white and quite hard. It was powdered with some difficulty in an agate mortar and resembled very much finely divided silica.

It was sometimes noted that the precipitate formed on passing the sulphur dioxide into the solution of zirconium chloride was partially dissolved upon the prolonged passage of the gas. To determine in how far the liberated hydrochloric acid was the agent causing this re-solution, some zirconium hydroxide, freshly precipitated by means of ammonium hydroxide, was washed free from hydrochloric acid and was then treated with a concentrated and freshly prepared solution of sulphur dioxide. This was allowed to stand during two or three months and was frequently shaken. The solid at the bottom of the flask separated into two layers, the gelatinous hydroxide settling first and upon this a white finely divided substance formed. The supernatant liquid was found to contain zirconium. The white layer was separated from the hydroxide and analyzed. It contained :

Zirconium dioxide .....	15.05	15.53	....
Sulphur dioxide.....	....	....	4.86
Water (blast-lamp).....	2.78	3.03	....
Water, at 95° C.....	77.41	76.33	....
	<hr/>	<hr/>	
	100.10	99.75	

Ratio of zirconium to sulphur dioxide is 2.2 : 1.

This substance apparently came to a constant weight on drying in a steam-bath at 95° C.

A somewhat peculiar product was obtained during an attempt at filtering the precipitated sulphite. It filtered very slowly and in the course of a few hours a layer of a watery liquid formed above the white sulphite. This was allowed to stand several days and turned into a solid jelly. This was noticed several times. The thickness of the jelly-like layer would, of course, depend upon the amount of moisture in the precipitate but several times it was half an inch or more in thickness. This body was analyzed in the moist condition after simply drying between filter-paper. It gave :

Zirconium dioxide.....	20.02	20.65	....	....
Sulphur dioxide.....	....	....	5.19	5.51
Water (blast-lamp).....	9.14	8.53	....	....
Water, at 95° C. ....	65.65	65.22	....	....
	<hr/>	<hr/>		
	100.00	99.91		

Ratio of zirconium and sulphur dioxide is here 3 : 1.

A portion of this jelly was brought to constant weight by heating for a number of hours in a steam-bath. About sixty-five per cent. of the original weight was lost and the body assumed a translucent appearance like dried gelatine. The analysis of this gave :

Zirconium dioxide.....	59.34	....
Sulphur dioxide .....	....	11.46
Water (blast-lamp) .....	29.20	...
	<hr/>	
	100.00	

Ratio of zirconium to sulphur dioxide is 4 : 1.

The analysis shows that some of the sulphur dioxide was lost on drying.

It will be seen then that these different preparations show a

very varying ratio of the zirconium to the sulphur dioxide and in no case approach to the ratio of the neutral sulphite (1 : 1.4). They are, therefore, to be looked upon as either mixtures of the sulphite and hydroxide or very unstable compounds. The jelly-like substance mentioned last gives more promise of being a chemical individual; still it has not been thought legitimate to attempt the calculation or assignment of a formula to it.

A last attempt at preparing the neutral sulphite was made by placing some of the excess of sulphurous acid, which had been standing over the precipitated zirconium sulphite, in a dessicator and allowing it to evaporate over sulphuric acid. The bulk of liquid decreased from about 200 cc. to five to ten cc. and then hard, white, warty crystals began to form, which were quite difficult to remove from the crystallizing dish. In appearance they resembled zirconium sulphate. The solution had lost the odor of sulphur dioxide. The time consumed in the evaporation was several months.

The crystals were dried upon filter-paper and yielded, on analysis,

Zirconium.....24.47 per cent.: on a dry basis, 36.43.

Sulphur dioxide 34.54      "      "      "      "      51.42.

Calculated for  $\text{Zr}(\text{SO}_3)_2$ , Zr 36.25;  $\text{SO}_3$  51.20. These crystals then seem to be a hydrated sulphite of the composition  $\text{Zr}(\text{SO}_3)_2 \cdot 7\text{H}_2\text{O}$ .

The nature of the precipitate gotten by means of sodium sulphite was also examined. The sulphite used was fairly pure. The zirconium chloride solution was distinctly acid and the mixed solution was acid. A transient precipitate was produced in the cold on mixing the two. On heating, a good flocculent precipitate was formed which settled well and was easily filtered. The precipitate looked like the hydroxide, rather than the white sulphite already described. The analysis gave:

Zirconium dioxide.....	5.75	5.75	....	....
Sulphur dioxide.....	....	....	1.05	1.004
Ratio of zirconium and sulphur dioxide is 4 : 1.				

Chancel<sup>1</sup>, in giving a method of separation of iron from zirconium, states that by means of a boiling solution of sodium thio-

<sup>1</sup> *Ann. d. Chem. u. Pharm.*, 108, 237; *Watt's Dictionary*, 5, 1081, 1877.

sulphate the zirconium is precipitated as thiosulphate. Stromeier<sup>1</sup> stated that if a dilute zirconium chloride solution be neutralized by sodium carbonate in the cold and sodium thiosulphate added until the solution was decolorized and then boiled as long as sulphur dioxide came off, the zirconium would be precipitated as oxide (meaning doubtless hydroxide).

To test these observations a solution of zirconium chloride was neutralized by ammonia and an excess of sodium thiosulphate was added in crystals. A precipitate began to be formed directly. This was washed eight or ten times by decantation, filtered, the precipitate dried by absorption paper, and analyzed. It gave:

Zirconium dioxide.....	19.66	20.50	....	....
Sulphur dioxide .....	....	....	4.03	4.14
Water (blast-lamp) .....	16.05	16.41	....	....
Water, at 95° C.....	60.11	58.58	....	....
	<hr/>	<hr/>		
	99.85	99.61		

Percentage of zirconium on a water-free basis is 75.

Percentage of zirconium calculated in  $Zr(S_2O_3)_2$  is 21.95.

A second experiment was carried out with an acid solution of zirconium chloride. The sodium thiosulphate crystals were added in the cold and when completely dissolved the solution was heated to boiling. This precipitate on analysis gave:

Zirconium dioxide.....	21.74	20.73	....	....
Sulphur dioxide.....	....	....	5.33	5.41
Water (blast-lamp).....	9.72	8.64	....	....
Water, at 95° C.....	63.28	65.37	....	....
	<hr/>	<hr/>		
	100.07	100.15		

Finally another portion was taken, precipitated with an excess of sodium thiosulphate, and boiled until there was no longer any odor of sulphur dioxide. This precipitate was analyzed:

Zirconium dioxide.....	47.01	47.19	....	....
Sulphur dioxide.....	....	....	6.90	6.95
Water (blast-lamp).....	21.41	21.14	....	....
Water, at 95° C.....	24.16	24.72	....	....
	<hr/>	<hr/>		
	99.48	100.01		

The low percentage of water here was due to the exposure of

<sup>1</sup> *Ibid.*, 123, 127.



the precipitate in a warm room and its consequent partial drying. There is no evidence here nor in the previous cases of the formation of any definite thiosulphate and we would question its existence under ordinary conditions. There is no evidence of the formation here of an hydroxide as one of the authors quoted states. Basic salts seem to be the only products.

UNIVERSITY OF NORTH CAROLINA,  
March, 1895.

---

### ON SOME CONDITIONS AFFECTING THE ACCURACY OF THE DETERMINATION OF POTASH AS POTAS- SIUM PLATINICHLORIDE.

BY A. L. WINTON, Connecticut Agricultural Experiment Station.

Received April 2, 1895.

IN the course of some determinations of potash in potassium chloride, made by direct evaporation with platinum solution preliminary to a further study of methods, it was observed that the potassium platinichloride was more finely divided and the results were higher when the solution of the potash salt was concentrated on adding the reagent, than when it was dilute.

In order to ascertain the real connections of the facts observed, I then made a series of experiments which were all conducted in exactly the same way, except for the kind of dish used, the dilution of the solution of potassium chloride on adding the platinum solution, the presence or not of added hydrochloric acid, the temperature of the water-bath, and the strength of alcohol used for washing.

The potassium chloride used was from a lot sent by Dr. H. J. Wheeler, Reporter on Potash, for the Association of Official Agricultural Chemists. After being finely ground, it contained 0.45 per cent. of moisture, which was determined by heating below a red heat over a lamp until constant weight was secured. In each case, approximately one-half gram was weighed out from a weighing bottle. After solution in water and adding platinum solution, the mixture was evaporated to a pasty condition, and about twenty-five cc. of alcohol were added and allowed to stand on the potassium platinichloride for one hour with repeated stirring. The precipitates were then collected in

Gooch crucibles, washed with about 100 cc. of alcohol, and dried to constant weight, first at 100° C. and finally at 130° C. The results calculated to potassium chloride by the use of the factor 0.3056 and expressed in per cents. of the quantity taken, are given in Table I.

It will be seen from the table that neither the kind of dish used, nor the temperature of the solution of potassium chloride on adding the platinum solution, nor the presence of a large excess of hydrochloric acid, during evaporation, nor the temperature of evaporation, had any perceptible influence on the results.

These points, therefore, need not be further considered. In most of the experiments ninety-five per cent. alcohol was used in order to diminish the solubility of the potassium platinichloride. In experiments Nos. 9, 10, 29, and 30, however, the alcohol was eighty per cent., and the results are, for this reason, somewhat lower.

*The Effect of Dilution of the Solution when Potassium Chloride with no Admixture is used.*—The principal point brought out by the experiments is the effect of the dilution of the potassium chloride solution when chloroplatinic acid is added, on the character of the potassium platinichloride, and the results.

If the potassium chloride were dissolved in fifty cc. of water, the potassium platinichloride was either not precipitated at all on addition of the platinum solution, or else went into solution when the liquid became heated, and was then deposited slowly on evaporation.

The potassium platinichloride thus obtained was invariably in brilliant, orange-colored granular crystals, which were often united to form plates from one to five mm. across. Constant weight was secured after drying the double salt for three hours at 100° C., the results of several determinations being concordant and slightly below theory. The loss on further drying at 130° was very small.

But if, on the other hand, ten cc. or less of water were used to dissolve the potassium chloride, a considerable portion of the potassium platinichloride precipitated as a fine powder immediately on adding the reagent, the remainder being deposited on evaporation. After treating with alcohol and filtering,

TABLE I.  
DETERMINATIONS OF POTASSIUM CHLORIDE UNDER VARIOUS CONDITIONS.  
(*Weight*  $K_2PtCl_6 \times 0.3056 = \text{weight } KCl.$ )

No. of experiment.	cc. water used to dissolve KCl.	cc. HCl concentrated added.	$H_2PtCl_6$ added to hot or cold solution.	Water-bath boiling or below boiling.	Volume per cent. of alcohol used for washing.	Kind of dish used for evaporation.	Grams of dry KCl taken.	Per cent. of KCl found.	
								$K_2PtCl_6$ dried at 100° C.	$K_2PtCl_6$ dried at 130° C.
1	50	0	Cold.	Boiling.	95	Porcelain.	0.4632	99.87	99.87
2	50	0	"	"	95	Platinum.	0.4582	99.84	99.86
3	50	0	Hot.	"	95	Porcelain.	0.4596	99.84	99.76
4	50	0	"	Below boiling.	95	Platinum.	0.4686	99.82	99.76
5	50	0	"	"	95	Porcelain.	0.4685	99.85	99.85
6	50	0	"	Boiling.	95	Platinum.	0.5194	99.82	99.85
7	50	2	"	"	95	Porcelain.	0.4682	99.87	99.85
8	50	2	"	"	80	Platinum.	0.4656	99.84	99.84
9	50	0	"	"	80	Porcelain.	0.4505	99.76	99.69
10	50	0	Cold.	"	95	Platinum.	0.5005	99.76	99.70
11	50	0	"	"	95	Platinum.	0.4463	100.17	100.01
12	25	0	Hot.	"	95	Porcelain.	0.4463	99.83	99.97
13	25	0	"	"	95	Platinum.	0.5107	99.64	99.77
14	25	0	Cold.	"	95	Porcelain.	0.5162	99.80	99.84
15	25	0	"	"	95	Platinum.	0.4582	99.06	99.93
16	25	2	Hot.	"	95	Porcelain.	0.5093	99.86	99.71
17	25	2	"	"	95	Platinum.	0.4643	100.06	100.80
18	25	2	Cold.	"	95	Porcelain.	0.4643	99.66	99.64
19	25	0	"	"	95	Platinum.	0.5371	100.35	100.04
20	25	0	Cold.	"	95	Platinum.	0.5185	100.37	100.16
21	10	0	Hot.	"	95	Porcelain.	0.4445	100.16	100.40
22	10	0	"	"	95	Platinum.	0.4445	100.16	100.08
23	8	2	Cold.	"	95	Platinum.	0.5186	100.56	100.14
24	8	2	Hot.	"	95	Porcelain.	0.4766	100.31	100.06
25	8	0	"	"	95	Platinum.	0.5082	100.45	100.19
26	5	0	"	"	95	Platinum.	0.5082	100.39	100.27
27	5	0	"	"	95	Porcelain.	0.5082	100.39	100.23
28	5	0	"	"	95	Platinum.	0.4612	100.47	100.23
29	5	0	"	"	95	Porcelain.	0.5093	100.26	100.30
30	5	0	"	Below boiling.	80	Platinum.	0.5060	100.09	99.95

the salt presented the appearance of a fine, yellow powder, with generally an occasional granular crystal. Constant weight at 100° was only secured after heating from nine to fifteen hours, the results, although not always concordant, being in every case considerably above theory. Heating for many hours at 130° C. further reduced the results, although even after this treatment they were still slightly above theory.

The difference in the results obtained in dilute and concentrated solutions, is brought out strikingly by the averages given in the following table :

TABLE II.  
AVERAGES OF RESULTS OBTAINED IN DILUTE AND CONCENTRATED SOLUTIONS OF POTASSIUM CHLORIDE.

Dilution of the solution on adding $\text{H}_2\text{PtCl}_6$ .	Vol. per cent. of alcohol.	Average of results of expts. — Nos. —	Per cent. KCl found.	
			$\text{K}_2\text{PtCl}_6$ dried at 100° C.	$\text{K}_2\text{PtCl}_6$ dried at 130° C.
50 cc.	95	1 to 9	99.84	99.82
10 cc. or less	95	19 " 29	100.38	100.17
50 cc.	80	9 and 10	99.77	99.69
5 "	80	29 " 30	100.20	99.98

The average of eight closely agreeing results, using fifty cc. of water and ninety-five per cent. alcohol and drying at 100° C. is 99.84 per cent. potassium chloride. After drying at 130° C. the average is only 0.02 per cent. lower. But where the conditions were the same, except that only ten cc. or less of water were used to dissolve the potassium chloride, the average of ten results is 100.38 per cent. potassium chloride, after drying at 100° C., and 100.17 per cent. or 0.21 per cent. lower, after drying at 130° C. The results after drying at 100° C. and 130° C. are, on an average, 0.16 and 0.18 per cent. respectively below theory, whereas in concentrated solutions they are 0.38 and 0.17 per cent. respectively, above theory.

The results, using eighty per cent. alcohol, although all rather lower, show similar differences.

In the cases where the potassium chloride was dissolved in twenty-five cc. of water the results generally agree with those where fifty cc. of liquid was present, although not always.

In Table III are given the per cents. of potassium chloride corresponding to the average losses in weight of the potassium

platinichloride during successive periods at 100° and 130° C., in the case of ten determinations using fifty cc. of water and of twelve using ten cc. or less of water.

TABLE III.

SHOWING THE AVERAGE RATE OF DRYING OF POTASSIUM PLATINICHLORIDE OBTAINED FROM DILUTE AND CONCENTRATED SOLUTIONS.

(The first heating of three hours at 100° C. is not considered.)

K <sub>2</sub> PtCl <sub>6</sub> heated at	Per cent. of KCl corresponding to loss in weight of K <sub>2</sub> PtCl <sub>6</sub> .	
	Dilute solutions. Average of expts. Nos. 1 to 11.	Concentrated solutions. Average of expts. Nos. 19 to 31.
100° C. 3 hours.....	0.019	0.062
3 " .....	0.003	0.036
3 " .....	0.003	0.022
3 " .....	0.000	0.003
Total....	0.025	0.123
130° C. 7 hours.....	0.025	0.088
7 " .....	0.006	0.058
7 " .....	0.000	0.035
7 " .....	0.000	0.020
7 " .....	0.000	0.010
7 " .....	0.000	0.003
Total.....	0.031	0.214
100° and 130° total.....	0.056	0.337

*The Effect of the Dilution of the Solution when Potassium Chloride with other Salts and Sulphuric Acid is used.*—Following a method, such as the so-called alternate method of the Association of Official Agricultural Chemists, the solution to which platinum solution is added, should contain only sodium and potassium chlorides, having been previously freed from other matters.

In experiments Nos. 33 and 34, in Table IV, the solution contains about one part of potassium chloride to one and one-half parts sodium chloride, which is the ratio of these salts in kainite, the richest in soda of the commercial potash manure salts. In experiments Nos. 35 and 36, the ratio of the two salts, is approximately as one to one-half.

In analyses by the Lindo-Gladding method, however, part or all of the potash may exist as sulphate in the solution to which platinum solution is added and sodium and magnesium sulphates and chlorides may also be present.

In experiments Nos. 37 and 38 about the same proportions of magnesium sulphate as would be present in kainite were added, and in experiments Nos. 39 and 40 two parts of sulphuric acid were added to one part of potassium chloride.

In all these experiments platinum dishes were used, no hydrochloric acid was added, the platinum solution was added to the hot solution of the salts, the evaporation was carried on over boiling water-baths, and eighty per cent. alcohol was used for washing. The quantities of potassium chloride taken varied from 0.24 to 0.50 gram. In the case of experiments Nos. 37 and 38, where magnesium sulphate was present, the potassium platinichloride, after being collected on Gooch crucibles, was washed with 150 cc. of Gladding's reagent,<sup>1</sup> and then with eighty per cent. alcohol.

The double salt was, in each case, not only dried at 100° and 130°, but also at 160° C. In other respects the work was conducted as described for previous experiments. Results are given in Table IV.

In these experiments the dilution of the solution had the same effect on the form of the potassium platinichloride, the rate of drying, and the results obtained as in those previously made on potassium chloride alone.

The granular crystals obtained from dilute solutions after drying for two hours at 100° did not lose more than 0.06 per cent. during subsequent heating of many hours at 100°, 130°, and 160° C., the pulverulent form precipitated in concentrated solutions, however, continued to lose in weight during successive periods of heating, the total loss being in no case less than 0.50 per cent. Determined in the presence of the same weight of the same kind of impurity the per cents. of potassium chloride calculated from the weight of potassium platinichloride dried at 100° C. are considerably higher when the solution was concentrated than

<sup>1</sup> A solution of one part of ammonium chloride in five parts of water which has been saturated in the cold with potassium platinichloride.

TABLE IV.

DETERMINATIONS OF POTASSIUM CHLORIDE IN DILUTE AND CONCENTRATED SOLUTIONS IN THE PRESENCE OF OTHER SALTS AND SULPHURIC ACID.

(The figures show the quantity of potassium chloride obtained, expressed in per cents. of the quantity taken. Weight  $K_2PtCl_6 \times 0.3056 = \text{weight } KCl$ .)

$K_2PtCl_6$ dried at—	Hours of drying.	KCl with no admixture.		KCl with 0.4 gram NaCl.		KCl with 0.2 gram NaCl.		KCl with 0.6 gram $MgSO_4$ .		KCl with 1 gram $H_2SO_4$ .	
		No. 31.	No. 32.	No. 33.	No. 34.	No. 35.	No. 36.	No. 37.	No. 38.	No. 39.	No. 40.
100° C.	2	0.5331 gram KCl in 50 cc. $H_2O$ taken.	0.5452 gram KCl in 4 cc. $H_2O$ taken.	0.2416 gram KCl in 25 cc. $H_2O$ taken.	0.2665 gram KCl in 2 cc. $H_2O$ taken.	0.3768 gram KCl in 37 cc. $H_2O$ taken.	0.3919 gram KCl in 3 cc. $H_2O$ taken.	0.4764 gram KCl in 50 cc. $H_2O$ taken.	0.4861 gram KCl in 4 cc. $H_2O$ taken.	0.4734 gram KCl in 50 cc. $H_2O$ taken.	0.4637 gram KCl in 4 cc. $H_2O$ taken.
	3	99.71	100.34	99.30	100.17	99.57	100.22	99.26	99.73	99.73	100.50
	5	99.71	100.21	99.30	100.07	99.57	100.07	99.25	99.67	99.73	100.42
	8	99.71	100.17	99.29	99.98	99.57	100.03	99.25	99.65	99.73	100.40
	11	99.70	100.11	99.29	99.98	99.57	99.99	99.25	99.64	99.73	100.32
	14	99.70	100.09	99.27	99.92	99.56	99.95	99.24	99.63	99.72	100.31
	17	99.70	100.08	99.27	99.90	99.56	99.93	99.24	99.63	99.72	100.29
	20	99.68	100.08	99.25	99.90	99.56	99.86	99.23	99.62	99.72	100.18
	26	99.68	99.91	99.25	99.74	99.55	99.75	99.23	99.46	99.72	100.14
	12	99.67	99.89	99.25	99.71	99.55	99.70	99.23	99.43	99.72	100.11
130° C.	18	99.67	99.89	99.25	99.62	99.55	99.67	99.23	99.42	99.72	100.09
	30	99.67	99.86	99.25	99.62	99.55	99.67	99.23	99.42	99.72	100.09
	36	99.67	99.86	99.25	99.62	99.55	99.67	99.23	99.42	99.72	100.09
	6	99.65	99.79	99.24	99.62	99.52	99.61	99.21	99.36	99.69	100.00
	18	99.65	99.72	99.24	99.62	99.52	99.61	99.21	99.36	99.69	99.95
	30	99.65	99.66	99.24	99.55	99.52	99.52	99.21	99.33	99.68	99.86
	42	99.65	99.63	99.24	99.54	99.51	99.50	99.21	99.20	99.68	99.81
160° C.	18										
	30										
Total loss exclusive of that during first 2 hours at 100		0.06	0.71	0.06	0.63	0.06	0.72	0.05	0.53	0.05	0.69

when it was dilute, but calculated from the weights after drying at  $160^{\circ}$  C. they are about the same.

Experiments Nos. 39 and 40 are practically equivalent to determinations on potassium sulphate with the addition of hydrochloric and sulphuric acids, the amount of the latter acid being about double that necessary to combine with the potassium to form the sulphate. Since in these experiments the results were practically the same as when no sulphuric acid was added, it is reasonable to assume that the effect of the dilution of the solution is the same whether the potash exists as chloride or sulphate.

In both dilute and concentrated solutions the results obtained in the presence of sodium chloride or magnesium sulphate, were lower than when determinations were made on potassium chloride with no admixture, or with only sulphuric acid.

In the presence of sodium chloride this was due partly, if not entirely, to the smaller quantity of potassium chloride taken. Since about the same amount of alcohol was used in all cases, the percentage error due to solubility of potassium platinichloride in alcohol would be greater, the smaller the quantity of the salt taken, although the actual weight lost might be the same.

In the two experiments where magnesium sulphate was present, the washing with Gladding's reagent and the second washing with alcohol undoubtedly increased the minus errors. Possibly the mere presence of sodium and magnesium salts depresses the results. The fact that the results are lower does not impair their value for the present purpose, as in each case the experiments with the same admixture were both made on nearly the same weight of potassium chloride and in exactly the same manner, except as regards the dilution of the solution.

*Results of Fresenius.*—R. Fresenius<sup>1</sup> in an article published in 1877 describing his method for determining potash as potassium platinichloride, directs to add platinum solution to a *concentrated* solution of the potash salt, wash with *eighty per cent. (by volume) alcohol*, and dry the potassium platinichloride to constant weight at  $130^{\circ}$  C.

In a later article<sup>2</sup> he gives the following results obtained by this

<sup>1</sup> *Ztschr. anal. Chem.*, 16, 63.

<sup>2</sup> *Ztschr. anal. Chem.*, 21, 238.



method on pure potassium chloride, with and without the addition of sodium chloride, using the factor 0.3056. He states that the potassium platinichloride was obtained in the form of a *fine powder*.

TABLE V.

RESULTS OF R. FRESENIUS ON POTASSIUM CHLORIDE WITH AND WITHOUT ADDITION OF SODIUM CHLORIDE.

(The figures show the quantity of Potassium Chloride obtained, expressed in per cents. of the quantity taken.  $Wt. K_2PtCl_6 \times 0.3056 = \text{weight. } KCl.$ )

Hours dried at 130°.	1.0378 gram KCl taken.	0.9563 gram KCl taken.	Hours dried at 130°.	0.9490 gram KCl and 0.1189 gram NaCl taken.	0.6812 gram KCl and 0.4524 gram NaCl taken.
2	100.67	100.42	5	100.19	100.13
7	100.40	100.16	8	100.11	100.06
12	100.23	100.04	11	100.04	99.98
21	100.19	100.00	14	100.02	99.97
30	100.10	99.93	20	100.00	99.94

The results of Fresenius without addition of sodium chloride are corroborated by my results in experiments Nos. 29 and 30 in Table I, and No. 32 in Table IV. In experiments Nos. 19 to 29, Table I, the results are a little higher, due to the lesser solubility of potassium platinichloride in ninety-five per cent. alcohol. The results given in Table IV, where sodium chloride was present, are somewhat lower than those of Fresenius, owing probably to the smaller weights of potassium chloride taken. If the factor, based on the latter and now generally accepted atomic weight of platinum as determined by Seubert, had been used, the results would be 0.42 per cent. higher.

There must be then some considerable plus error which more than compensates for the errors due to the solubility of the salt in alcohol and the use of the wrong atomic weight of platinum. This error is largely attributable to the presence of water in the potassium platinichloride.

Seubert<sup>1</sup> finds that it is difficult to so prepare this salt that it will be free from "*verknisterungs wasser*," which is not completely removed even at 160° C. The slow drying of the pulverulent potassium platinichloride at 100° C., and the further loss in weight after subsequent drying at 130° C. is in harmony with Seubert's experience. The results after drying for many hours

<sup>1</sup> Ann. Chem., 207, 1.

at  $130^{\circ}$  C. are very close to theory, where eighty per cent. alcohol was used, notwithstanding the solubility of the salt, and are higher if the alcohol were ninety-five per cent.

*Microscopic Examination of the Potassium Platinichloride.*—It has been already stated that the potassium platonic salt, when deposited on evaporation of dilute solutions, was coarsely crystalline, while obtained from concentrated solutions, it was finely pulverulent. Examined under the microscope, the difference was even more striking. The coarse form was found to consist of octahedrons, generally attached to one another, forming thin plates, and corresponded to the descriptions usually given in the books, but when the salt was pulverulent, it consisted largely of curious radiating crystals, a characteristic form consisting of three bars intersecting at right angles to each other. Resting on three of the six arms, they presented at first sight, the appearance of stars with six arms in the same place, but by careful focussing, their true form was revealed.

Prof. S. L. Penfield, of Yale University, has very kindly examined my precipitates, and reports as follows :

Both forms of crystals belong to the isometric system. The coarse crystals being deposited slowly, are normal octahedrons; the pulverulent crystals, however, owing to their rapid formation, are very much distorted being developed into rods, crossing at  $90^{\circ}$ , parallel to the direction of the isometric axes.

In both the octahedrons and the interpenetrating rods, there were globular cavities which, before drying, were undoubtedly filled with mother-liquor. Only an occasional cavity could be seen in the octahedrons, but in the rods they were very abundant.

Even after the long continued heating at  $130^{\circ}$  C. ocular proof was secured that the octahedrons were not entirely dry. Patient search revealed the presence of minute cavities from 0.003 to 0.01 mm. across, which were still partially filled with liquid. On inclining the stage about  $45^{\circ}$  and revolving it about its center, a bubble could be seen to move from one side to the other exactly as the bubble moves in a spirit level.

The facts disclosed by Prof. Penfield's examination, explain the slow drying in my experiments. The octahedrons, being comparatively free from inclosed liquid, did not lose greatly in

weight on heating; the interpenetrating rods, however, contained a very considerable amount of inclosed liquid, part of which was slowly given off on heating at  $100^{\circ}$ , more at  $130^{\circ}$ , and still more at  $160^{\circ}$  C.

The quantity of liquid enclosed in the octahedrons could not have been considerable, but it shows the persistence with which water, once enclosed, is retained.

*Conclusions.*—The method of precipitating in concentrated solutions, and drying the potassium platinichloride at  $130^{\circ}$  depends, for its accuracy, on the compensation of three errors, due (1) to the solubility of the potassium platonic salt in eighty per cent. alcohol, (2) to the presence of water in the crystals which is not driven off at  $130^{\circ}$ , and (3) to the use of a factor based on the wrong atomic weight of platinum. Such a method is certainly open to criticism. The solubility in alcohol occasions an error that can hardly be avoided. It could be diminished by using ninety-five per cent. alcohol, but further experiments would be necessary in order to ascertain whether for other reasons the stronger alcohol could be advantageously substituted for the weaker.

The results given herewith show that *the error occasioned by the presence of water can be greatly reduced and the process of drying simplified, by adding the platinum solution to a dilute solution of the potash salt (one part of potassium chloride or six-tenths part potassium oxide to 100 cc. of water) and drying the potassium platini-chloride at  $100^{\circ}$  C.* It is not claimed that the double salt thus obtained is perfectly dry, but it is necessary to heat the pulverulent form for many hours at  $160^{\circ}$  C. in order to secure it as free from water as the granular crystals obtained by the above simple process.

The liquid enclosed in the crystals, although largely water, must contain also solid matters, which remain behind, however complete may be the drying. It must then follow that the less liquid inclosed at the outset, the smaller the error due to this cause after drying.

With such a simple method at our disposal for obtaining the potassium platonic salt comparatively free from moisture, the necessity for using an erroneous factor at once disappears.

The factors based on the atomic weights as revised by F. W.

Clarke<sup>1</sup>, up to January 1, 1894, would be 0.30688 for potassium chloride, and 0.1939 for potassium oxide. These factors would make all the foregoing results 0.42 per cent. higher in potassium chloride, which is equivalent to 0.26 per cent. higher in potassium oxide.

In Table VI are given comparative results by the old and new factors, in the cases of all the preceding experiments in which one part of potassium chloride was dissolved in approximately 100 parts of water, and the potassium platinichloride was washed with eighty per cent. alcohol and dried two or three hours at 100° C.

TABLE VI.

COMPARISON OF RESULTS OBTAINED BY THE FACTORS 0.3056 AND 0.30688 FOR CALCULATING POTASSIUM CHLORIDE FROM POTASSIUM PLATINICHLORIDE.

(*Chloroplatinic Acid added to Dilute Solutions of Potassium Chloride, Potassium Platinichloride washed with eighty per cent. Alcohol and dried two to three hours at 100° C.*)

Expt. No.	Material taken.	Per cent. KCl found using factor.	
		0.3056	0.30688
9	0.4500 gram KCl.....	99.77	100.19
10	0.5005 gram KCl.....	99.76	100.18
31	0.5331 gram KCl.....	99.71	100.13
33	0.2416 gram KCl and 0.4 gram NaCl .....	99.30	99.72
35	0.3768 gram KCl and 0.2 gram NaCl.....	99.57	99.99
37	0.4764 gram KCl and 0.6 gram MgSO <sub>4</sub> .....	99.26	99.68
39	0.4734 gram KCl and 1.0 gram H <sub>2</sub> SO <sub>4</sub> .....	99.73	100.15

It will be seen that when potassium chloride, either alone, or mixed with sulphuric acid was taken, the results using the factor 0.30688 are 0.13 to 0.19 per cent. above theory. This would indicate either that the water remaining in the double salt after drying for two or three hours at 100° C. a little more than compensated for the solubility in alcohol, or else that there are other slight plus errors.

When, however, other salts are present, and particularly if

<sup>1</sup> U. S. Dept. Agr., Chem. Div., Bull. 43, p. 340.

Potassium = 39.11.

Platinum = 195.00.

Oxygen = 16.00

Chlorine = 35.45.

the Gladding method were followed, the tendency is toward lower results.

Taken as a whole the new factor gave, in these instances, more satisfactory results than the old factor.

A method which so reduces the error due to inclosed water in the double salt, that it about compensates for the solubility in alcohol, and which employs the factor based on the revised atomic weights, is, in my opinion, to be preferred to one which depends, for the accuracy of results, on the compensation of three errors, one of which is due to the use of a factor known to be incorrect, especially when the former method gives more concordant results and is more readily carried out.

*Summary.*—When chloroplatinic acid was added to a concentrated solution of potassium chloride, a large part of the potassium platnichloride formed was precipitated at once in a pulverulent form, the remainder being deposited on evaporation. After treating with alcohol, filtering, and drying, the double salt was in a fine powder which, examined under the microscope, was found to consist largely of radiating crystals, a characteristic form having six arms, formed by the intersection at right angles of three bars. Numerous globular cavities in the crystals gave evidence that during their rapid formation mother-liquor was enclosed. Owing to this enclosed liquid the double salt dried slowly at  $100^{\circ}$ , lost further in weight after heating subsequently for many hours at  $130^{\circ}$ , and further still at  $160^{\circ}$  C. The loss at these temperatures compared with the weight after drying three hours at  $100^{\circ}$ , was equivalent to about six-tenths per cent. potassium chloride.

When, however, the solution of the potash salt was so dilute that no precipitate was formed on adding the reagent, the potassium platinic salt being deposited on evaporation, the latter was obtained in octahedrons, generally attached to one another forming crystalline plates. These octahedrons were comparatively free from cavities, and practically the same results were secured after drying three hours at  $100^{\circ}$ , as after drying for many hours at  $130^{\circ}$  and  $160^{\circ}$  C.

Somewhat lower results were obtained in the presence of sodium chloride and magnesium sulphate, whatever the dilution of the

solution, but in other respects the above statements will hold true.

The kind of dish used, the temperature of the evaporation, the presence of free hydrochloric acid and free sulphuric acid, did not appear to influence the results.

A method based on the evaporation of dilute solutions, drying the potassium platinichloride at  $100^{\circ}$ , and the use of the factors 0.30688 for potassium chloride and 0.1939 for potassium oxide, gave good results and is believed to be more satisfactory for scientific and practical reasons, than the method of Fresenius, in which the platinum solution is added to concentrated solutions, the double salt is dried many hours at  $130^{\circ}$  C. and the factors 0.3056 and 0.19308 are used.

## THE INDIRECT ANALYSIS OF MIXTURES CONTAINING A COMMON CONSTITUENT.

BY EDWARD K. LANDIS.

Received March 15, 1895.

### FIRST METHOD.

**C**ALCULATION of mixtures containing a common constituent.

*Data given :*

Weight of mixture.

Weight of common constituent in mixture.

Let  $x$  = one salt.

Let  $y$  = the other.

Let  $a$  = amount of common constituent in one part of  $x$ .

Let  $b$  = amount of common constituent in one part of  $y$ .

Let  $z$  = weight of mixture.

Let  $Q$  = weight of common constituent in mixture.

To find values of  $x$  and  $y$ ;

$$x + y = z.$$

$$ax + by = Q.$$

$$a(z - y) + by = Q.$$

$$az - ay + by = Q.$$

$$by - ay = Q - az.$$

$$y = \frac{Q - az}{b - a} \text{ and } x = z - y.$$

## SECOND METHOD.

Same data. Calculate the weight of salt of greatest molecular weight if entire amount of common constituent were combined with it. Subtract from this the weight of the mixture. This difference is proportional to the amount of salt of least molecular weight contained in the mixture. Therefore, form the proportion

$$\left( \begin{array}{c} \text{Molecular weight} \\ \text{heaviest} \end{array} \right) - \left( \begin{array}{c} \text{Molecular weight} \\ \text{lightest} \end{array} \right) : \left( \begin{array}{c} \text{Difference} \\ \text{found above} \end{array} \right) \\ :: \left( \begin{array}{c} \text{Molecular weight} \\ \text{lightest} \end{array} \right) : x.$$

$x$  = amount of salt of least molecular weight contained in the mixture.

## INDIRECT ANALYSIS.

*Example. Method No. 1.*—A sample of  $\text{NaHCO}_3$ , containing  $\text{Na}_2\text{CO}_3$ , gave 97.21 per cent. of the mixed carbonates, and 50.98 per cent of  $\text{CO}_2$ .

$$\text{NaHCO}_3 = 0.5238095 \text{ CO}_2.$$

$$\text{Na}_2\text{CO}_3 = 0.4150943 \text{ CO}_2.$$

$$\text{Let } x = \text{per cent. NaHCO}_3.$$

$$\text{Let } y = \text{per cent. Na}_2\text{CO}_3.$$

$$\text{Then } a = 0.5238095.$$

$$b = 0.4150943.$$

$$z = 97.71.$$

$$Q = 50.98.$$

$$x + y = 97.71.$$

$$x = (97.71 - y).$$

$$0.5238095x + 0.4150943y = 50.98.$$

$$0.5238095(97.71 - y) + 0.4150943y = 50.98.$$

$$51.1814 - 0.5238095y + 0.4150943y = 50.98.$$

$$0.1087152y = 0.2014.$$

$$y = 1.85254 = \text{per cent. Na}_2\text{CO}_3.$$

$$x = 95.85746 = \text{per cent. NaHCO}_3.$$

Proof:

$$\begin{array}{r} 1.85254 \times 0.4150943 = 0.76897 \\ 95.85746 \times 0.5238095 = 50.21104 \\ \hline 50.98001 \end{array}$$

*Example. Method No. 2.*—Same data as before.

Molecular weight.	Molecular weight.	Amount NaHCO <sub>3</sub> .
CO <sub>2</sub> : per cent. CO <sub>2</sub> found =	NaHCO <sub>3</sub> : $x$ .	
44 :	50.98	= 84 : 97.3255.

$$97.71 - 97.3255 = 0.3845.$$

$$\left( \begin{array}{c} \text{Molecular weight} \\ \text{Na}_2\text{CO}_3 \end{array} \right) - \left( \begin{array}{c} \text{Molecular weight} \\ \text{NaHCO}_3 \end{array} \right) : \left( \begin{array}{c} \text{Difference} \\ \text{found} \end{array} \right)$$

$$= \left( \begin{array}{c} \text{Molecular weight} \\ \text{Na}_2\text{CO}_3 \end{array} \right) : \left( \begin{array}{c} \text{Per cent. Na}_2\text{CO}_3 \\ x \end{array} \right)$$

$$22 : 0.3845 = 106 : 1.852.$$

Na<sub>2</sub>CO<sub>3</sub> = 1.852 per cent.

NaHCO<sub>3</sub> = 95.858 per cent.

Proof:

$$\begin{array}{r} 1.852 \times 0.4150943 = 0.76875 \\ 95.858 \times 0.5238095 = 50.21133 \\ \hline 50.98008 \end{array}$$

### ACCURACY OF THE DYEING TEST.

BY CHARLES S. BOYER.

Received April 8, 1895.

THE accuracy and value of the laboratory dyeing test of the natural organic dyestuffs, such as logwood, etc., is a much mooted question among those engaged in the dye-stuff trade. Some hold that the dyeing test is only of value where the dyestuff is to be used in exactly the same manner as the laboratory test, and since about every dyer has his own modifications of the general method of dyeing with the dye-stuff the test is useless except for special cases. Still others hold that the dyeing test never gives the actual value of the dyestuff.

To ascertain the accuracy of the dyeing test the writer made a series of comparative dyeing tests, and also analyzed the dye-stuffs according to the best methods of analytical chemistry now known. For these tests several samples of logwood and extract of sumac were used.

*Logwood.*—Fifty grams each of two different samples of thoroughly dried chipped "St. Marc" logwood were repeatedly extracted with water and the weak liquor evaporated to one



liter, care being taken to remove all insoluble matter from the solution. A number of skeins of worsted yarn, of five grams each, were mordanted in separate baths containing 0.150 gram potassium bichromate and 0.075 gram potassium tartrate in 500 cc. water. Two of these skeins were dyed respectively in baths containing thirty-five cc. of each extract, when it was found that sample No. 1 was considerably stronger than No. 2. Dyeing tests were now made, using varying amounts of No. 2 and thirty-five cc. of No. 1, with the result that thirty-five cc. of the latter were equal to forty-five cc. of No. 2, from which we find that 100 parts No. 1 equal, in tinctorial value, 128.5 parts No. 2.

One hundred cc. of each extract solution were now filtered through thoroughly washed hide powder, as described by L. Schreiner (*Chem. Ztg.*, 1890, 961), and the filtrate evaporated to dryness and dried at 100° C. until constant weight is obtained. One hundred cc. of each of the original solutions were also evaporated to dryness and dried at 100° C., the difference in the weights being the coloring matter removed. The results were:

	No. 1. Gram.	No. 2. Gram.
Weight of residue from 100 cc. of the original solution after evaporating to dryness.....	0.6110	0.4714
Weight of the dry residue from 100 cc. of the original solution after being filtered through hide powder.....	0.0368	0.0313
Weight of coloring matter.....	0.5742	0.4401

from which we find that 100 parts No. 1 equal, in tinctorial value, 130.4 parts No. 2.

Another experiment was made to ascertain the accuracy of the Schreiner method, using a sample of hematein which had been made by the writer from chipped logwood.

Five grams of this pure, powdered, and dried hematein were dissolved in one liter of water and 100 cc. of the solution run through hide powder, and the filtrate evaporated to dryness. Results:

(1) Hide powder removed from 100 cc. of original solution, 0.4989 gram. Theory, 0.5000 gram.

(2) Hide powder removed from 100 cc. of original solution, 0.4991 gram. Theory, 0.5000 gram.

This shows that hide powder will remove practically all of the coloring matter of logwood.

It may be well to mention just here, that while the Schreiner method is accurate when working on pure extracts and chipped woods, it is absolutely worthless so far as giving the percentage of hematein and hematoxylon in extracts adulterated with quercitron bark, tannin-containing compounds, etc.

The hide powder treatment extracted 0.965 gram of matter from 100 cc. of a fifty per cent. hematein and fifty per cent. tannin solution, while theory required but 0.500 gram of hematein.

Trimble's volumetric method of the color reaction given by two samples, when treated with copper sulphate, gave a dilution of 100 cc. for No. 2 to 127 cc. for No. 1, which indicates that 100 parts No. 1 are equal to 127 parts No. 2.

The above results show that a dyeing test, when applied to chipped logwoods and unadulterated extracts of logwood, yield results that will compare favorably with most of the methods used in analytical chemistry.

*Extract of Sumac.*—A series of dyeing tests were also made upon six samples of extract of sumac which came to me in the ordinary course of business.

The dyeing tests were made as follows: one and a half grams of each extract were diluted with water to 500 cc., and then a five gram skein of "boiled out" cotton yarn was "laid down" in each bath over night. The temperature of the baths during the night was the ordinary room temperature. The next morning each skein was taken out of the bath and all wrung out as nearly alike as possible. Baths, equal in number to that of the skeins, were made containing two and one-fourth grams of ferrous sulphate to 500 cc. of water, and the skeins "entered" cold and turned for thirty minutes when the solutions were brought to a boil in a water-bath and held there one hour. The skeins are now taken out, rinsed, and dried. After several trials, varying the amount of extract in each bath, it was found that the following amounts gave shades which were of the same depth and intensity:

Sample No. 1657 .....	2.011 grams or 134 parts.
" " 1661 .....	1.830 " " 122 "
" " 1662 .....	1.575 " " 105 "
" " 1663 .....	1.800 " " 120 "
" " 1665 .....	2.200 " " 146.7 "
" " 1666 .....	1.500 " " 100 "

This shows that 100 pounds of No. 1666 will do the same work as 134 pounds of No. 1657, or 146.7 pounds of No. 1665, etc.

Now of each extract four to eight grams were weighed out and dissolved in one liter of water, and the tannin determined in them by the hide powder method as described in Allen's Commercial Organic Analysis, 3, Part 1, 119. The results are as follows:

No.	Specific gravity.	Total solids. Per cent.	Tannin. Per cent.	Non-tannin. Per cent.	Relative value in parts.
1657.....	1.2445	45.91	18.50	27.41	136.1
1661.....	1.2741	49.51	20.99	28.52	119.9
1662.....	1.2849	51.32	23.48	27.84	107.2
1663.....	1.2648	49.11	21.03	28.08	119.7
1665.....	1.2738	49.14	17.30	31.84	145.5
1666.....	1.2438	45.27	25.18	20.09	100.0

A comparison of these results with those obtained upon the same samples by means of the dyeing test shows a very close and favorable agreement.

While the hide powder method is not all that could be desired in the line of accuracy, yet, in the present knowledge of the chemistry of the tannins, it is the best method we have for the valuation of such extracts as are used on account of their tannin contents. This method also yields results which are much nearer the practical value, and can, in all fairness, be used as the standard in the valuation of extracts by the dyeing test.

The results of the above investigation are: First, the dyeing test yields results which compare favorably in accuracy with the best methods of analytical chemistry. Second, that the results of the dyeing test have a practical value.

Another feature of the dyeing test applied to the natural organic dyestuffs is, that it will frequently show not only any admixture with other dyestuffs, but also give an indication of the method employed in their manufacture. Suppose, for example, one of the extracts of sumac had been adulterated with

extract of quercitron bark. Such an addition would have been indicated by the modification of the shade given with ferrous sulphate. Again, had the extract of logwood been oxidized with hydrogen peroxide, etc., the color would have been taken up by the wool fiber much quicker and the deep blue shade would have developed much sooner than with an extract not so oxidized.

CAMDEN, N. J., April, 6, 1895.

### ABSORBENT BLOCKS.<sup>1</sup>

BY PETER T. AUSTEN AND W. HOMER BROADHURST.

Received April 16, 1895.

FOR drying moist precipitates unglazed plates are generally used in the laboratory, but they have the disadvantages of being rather expensive, as well as fragile, while their absorptive capacity is not great.

We have found that a mixture of equal parts of infusorial earth and plaster of Paris, when moistened, will set, forming a block that after drying has a very strong absorbent power for liquids. The plaster and infusorial earth are thoroughly mixed, then moistened with sufficient water to work easily, and placed in the molds. After setting, the blocks are placed in an air-chamber and heated for a day or two at 100°–120° to free them from hygroscopic moisture.

The molds are easily made in the following way: A sheet of glass, the larger the better, is laid on a table, and rubbed with waste oiled with a few drops of light lubricating oil. Long glass strips, an inch wide, and one-quarter of an inch or more thick, are laid on edge on the plate at a distance apart of six inches, if the block is intended to be of that size, and cross-pieces of the same kind of glass strips, but cut in suitable lengths, are placed between the long parallel strips, thus making squares. The strips should also be oiled a little. The wet mixture is poured in and the top smoothed with a straight edge of wood. After setting, the strips of glass are easily removed and the blocks come off the plate easily, and are ready to be placed in the drying oven. The surface next to the glass plate is very smooth.

<sup>1</sup> Read before the N. Y. Section, March 8, 1895.

These blocks are very convenient in qualitative analysis, and in the preparation of substances. The filter-paper containing the wet precipitate; or substance to be dried, is placed on the smooth side of the block, and after a short time much of its moisture is absorbed. One or more filter-papers may be placed between the substance and the block if too intimate contact of the substance and the block be not desired.

CHEMICAL LABORATORY OF THE BROOKLYN  
POLYTECHNIC INSTITUTE.

## THE VOLUMETRIC DETERMINATION OF ZINC AND A NEW INDICATOR FOR FERROCYANIDE.<sup>1</sup>

BY GEORGE C. STONE.

Received March 11, 1895.

**B**EFORE titrating with ferrocyanide it is necessary to separate all the metals of the iron group. Rapid and accurate methods are known for all but manganese; the methods commonly used in gravimetric analysis take too long; and I have been unable to get even passably accurate results on the New Jersey ores by the method of Messrs. von Schultz and Low,<sup>2</sup> or the modification of it proposed by Mr. Hinman.<sup>3</sup> Not finding any satisfactory method of separation I have tried titrating the two together, determining the manganese in a separate portion, by titration with permanganate, and taking the zinc by difference, and find the method easy, rapid, and sufficiently accurate for technical work.

*Indicators.*—Uranium salts are generally used as indicators for ferrocyanide and are fairly satisfactory when titrating zinc alone, though the sensitiveness of the test varies very much with the amount of free acid present. In titrating manganese, uranium cannot be used in the usual manner because it reacts on the precipitated manganese ferrocyanide; good results can be obtained by its use by putting drops of the solutions to be tested, on filter-paper and allowing them to run together so that the uranium does not touch the precipitate; the reaction develops very slowly making the titration very tedious. Ferric chloride, another

<sup>1</sup> Read before the N. Y. Section, March 9, 1895.

<sup>2</sup> Colorado Scientific Society, June 11, 1892; *J. Anal. Appl. Chem.*, 6, 682.

<sup>3</sup> S. of M. 2, 14, No. 1; *J. Anal. Appl. Chem.*, 6, 682.

commonly used indicator, proved entirely unsuitable. Copper sulphate was found to be about as delicate as uranium, but open to the same objections. Cobalt nitrate was by far the best indicator tried; the delicacy of the reaction is not affected by as much as one part of concentrated hydrochloric acid in fourteen of water; the reaction shows instantly and cobalt does not react on the precipitates. The cobalt solution should be quite dilute; a drop of it is placed on a white porcelain plate, and a drop of the solution to be tested by it, so that the drops touch but do not mix; an immediately shown faint greenish line, at the junction of the two, marks the end reaction. If the drops mix it is impossible to see the reaction; if the color does not show at once the end is not reached. Often when near the end the color will show after standing a few seconds, but at the actual end-point it shows as soon as the drops touch.

Manganese must be titrated at the ordinary temperature of the laboratory; at higher temperatures the amount of ferrocyanide used varies with the temperature. The composition of the precipitate is not normal, but is  $Mn_3Cf_4$ ; that is, an amount of ferrocyanide that will precipitate four atoms of zinc will only precipitate three of manganese.

*Ferrocyanide Solution.*—The best strength was found to be about thirty grams to the liter. It is standardized by titrating solutions containing known amounts of zinc or manganese, using about one-tenth gram, making slightly acid with hydrochloric acid and keeping the solution at about the volume used in the analysis.

The amount of ferrocyanide necessary to give a reaction with cobalt in this volume of acidulated water must be determined, and the amount so found deducted for each titration; it is about seven-tenths cc. for a volume of 140 cc.

*Permanganate Solution.*—1.99 grams of crystallized potassium permanganate to the liter gives a solution, one cc. of which equals 0.001 gram of manganese. It is standardized in the usual manner by iron, and the strength obtained by multiplying the iron value by 0.294646 (ten iron equals three manganese).

Sulphide ores are best dissolved in hydrochloric acid and potassium chlorate, taking care to have sufficient acid present to

keep all the manganese in solution. Oxides, carbonates, and silicates can be dissolved in hydrochloric acid and oxidized by boiling with potassium chlorate. Ores containing franklinite or rhodonite must be fused with sodium carbonate and evaporated to dryness with hydrochloric acid to decompose them thoroughly, then taken up with a slight excess of hydrochloric acid, and boiled with potassium chlorate to oxidize the iron.

Lead alone need not be separated; copper can be precipitated by lead; or lead and copper can both be precipitated by aluminum. Cadmium, if present, must be precipitated by hydrogen sulphide and the solution oxidized after filtering out the precipitate.

Iron and alumina are best separated by barium carbonate; the solution should, preferably, not contain a very large amount of free acid; the iron must all be ferric; the solution must not be warmed and, most important, the barium carbonate must be entirely free from alkaline carbonates and hydroxides, barium hydroxide, and ammonium salts. No barium carbonate in the market answers these requirements, but the ordinary chemically pure salt can easily be purified so that it answers perfectly. Select a salt that is free from ammonia (*e. g.*, Merck's), suspend it in water, and warm for several hours with two or three per cent. of its weight of barium chloride; this converts the alkaline carbonate present to chloride; the small excess of soluble barium salt does not interfere.

The thoroughly oxidized solution of the ore should be washed into a 500 cc. flask, cooled, and barium carbonate, suspended in water, added until the precipitate curdles; an excess of barium does no harm. The change in the appearance of the precipitate is very marked. Pour into a beaker, mix thoroughly, let it settle, decant the clear liquid through a dry filter, and take portions of 50, 100, or 200 cc. for each titration. The solution must be filtered from the iron at once and should be titrated as soon as filtered. If it be necessary to let the solution stand it must be made slightly acid or some zinc will precipitate. One portion, which should contain between 0.01 and 0.04 gram of manganese, is diluted to about 200 cc., heated nearly to boiling in a white porcelain dish, and titrated rapidly with permanganate

with very vigorous stirring. The greater part of the permanganate necessary should be added as rapidly as possible or the manganese oxide is apt to stick to the sides of the dish, making it difficult to see the pink color of the solution at the end. To obtain satisfactory results, the titration must be performed rapidly, so that, if the percentage of manganese be not approximately known, it is better to make a preliminary titration, adding one or two cc. at a time.

In a second portion, made slightly acid<sup>1</sup> with hydrochloric acid, the zinc and manganese are titrated together cold by ferrocyanide; if the manganese be present in appreciable quantity the color of the precipitate will darken as the ferrocyanide is run in and quite suddenly change to a light greenish yellow shortly before the end is reached. It is not necessary to begin to test the solution with cobalt until one or two cc. after the lightening of the precipitate; it should then be tested after the addition of each few drops. If there be little or no manganese present and the percentage of zinc be not approximately known, it saves time to make a preliminary titration, adding one or two cc. at a time. If lead be present the solution must be made quite strongly acid<sup>1</sup> before titrating to prevent the lead from being precipitated as ferrocyanide; five cc. of hydrochloric acid in 100 cc. of solution is sufficient.

The calculation of the results is best shown by an example: One cc. of the ferrocyanide used equaled 0.00606 gram of zinc or 0.00384 gram of manganese; one cc. of the permanganate equaled 0.001 gram of manganese; two and one-half grams of the ore were dissolved and the iron precipitated and filtered out as described above; fifty cc. of the solution was diluted, heated, and titrated with permanganate, requiring 18.45 cc., equal to 7.38 per cent. of manganese. 100 cc. titrated with ferrocyanide required 27.85 cc. The previous titration had shown that there was 0.0369 gram of manganese present which would require 9.61 cc. of ferrocyanide; deducting this left 18.24 cc. for the zinc, equal to 0.11053 gram, or 22.11 per cent.

<sup>1</sup> Manganese ferrocyanide is soluble in a large excess of hydrochloric acid, which should therefore be avoided; or the results will be low if much manganese be present. Five cc. of concentrated hydrochloric acid added to 100 cc. of a solution containing 0.05 gram of manganese did not cause any appreciable error. Ten cc., however, prevented the precipitation of any manganese.



This method has been used for some months in the laboratory of the New Jersey Zinc and Iron Co., with very satisfactory results. The following table shows how this compares with the ordinary gravimetric methods.

Material Analyzed.	Zinc		Manganese	
	Gravimetric.	Volumetric.	Gravimetric.	Volumetric.
N. J. ore.....	22.05	22.11	7.58	7.38
" " .....	26.58	26.48	N. D.	11.98
Brass.....	5.06	5.12	O.	O.
N. J. ore.....	22.50	22.47	N. D.	11.55
" " .....	30.75	30.82	"	7.54
Blende .....	38.28	38.18	"	0.14
Willemite .....	55.55	55.68	O.	O.
Residuum .....	4.60	4.79	12.23	12.30
" .....	4.29	4.44	N. D.	11.99
" .....	9.15	8.99	"	11.61
Tailings .....	2.12	2.05	6.04	6.00
Middles .....	15.15	15.24	9.24	9.14

In conclusion I wish to express my thanks to Mr. D. A. Van Ingen, who has done much of the experimental work necessary in testing the method.

### SOME PHYSICAL ASPECTS OF THE NEW GAS, ARGON. THE IDEAL THERMOMETRICAL SUBSTANCE FOR HIGH TEMPERATURES.

By W. R. QUINAN.

Received March 31, 1895.

**T**HE discovery, by Lord Rayleigh and Professor Ramsay, of a new gaseous constituent of the atmosphere, has a many-sided bearing upon science and excites the interest of the whole world.

While there may be mooted questions yet to be decided in regard to the elementary constitution of argon, certain extraordinary conclusions seem to have been reached. In the sense of the kinetic theory, it is a monatomic gas; that is, if heat be applied to it, all or very nearly all of this heat will be expended in dynamic energy. The kinetic theory, whatever may be its shortcomings, is certainly the most intelligible hypothesis now at our command, both to explain and to expound the ideal behavior of matter in its simplest form—the gaseous. The behavior, it must be remembered, is independent of the theory. It is the fruit of experimental research.

According to the kinetic theory, in a monatomic gas the ratio of the specific heat under constant pressure to the specific heat at constant volume is one and two thirds. In diatomic gases, some of which are sufficiently normal in their behavior at ordinary temperatures to allow the experimental ratio to be taken as the theoretical—this ratio is about 1.41. In triatomic gases the theoretical ratio is 1.273, and so on according to a relation applicable to all molecules except monatomic

$$\gamma = 1 + \frac{0.41}{\frac{1}{2}N} \quad (a)$$

in which  $\gamma$  is the ratio and  $N$  the number of atoms in the molecule.

The kinetic view is briefly as follows: A gas consists of discrete molecules endowed with energies. Of these, the dynamic energy, referred to the units of space and time, is measured (under the condition of uniform distribution) by the pressure. This is due to the motions of the molecules as entities. But the molecule itself is usually a complex system, consisting of two or more united atoms. The parts of this secondary system are capable of rotation about their center of mass and, perhaps, of various other movements, such as vibrations of the constituent atoms. The energy absorbed by the motions of this secondary system (under the condition of rest for the center of mass) may be called for simplicity the internal energy, while that due to the movement of the molecule as a whole may be called the kinetic. According to the conception and the laws of mechanics, the "free path" of a molecule is rectilinear. By encounters or collisions between the molecules there is a constant exchange and redistribution of the energy between these two forms of energy, but for every gas (in the ideal state) a constant ratio is preserved between the two forms, and each form, therefore, preserves a constant ratio to the whole energy.

In all gases, the ratio  $\beta$  of the whole energy to the kinetic, bears a simple relation to  $\gamma$ , the ratio of the specific heats, as follows:

$$\beta = \frac{2}{3(\gamma - 1)} \quad (b) \qquad \gamma = 1 + \frac{2}{3\beta} \quad (c)$$

Combining (b) with (a) above we have

$$\beta = \frac{N}{1.23} \quad (d)$$

This formula (d) like (a), from which it is derived, applies to all molecules except monatomic.

In a monatomic gas the only energy which can be absorbed by the molecule (single atom), considered at rest with respect to its center of mass, is one of rotation. On account of the infinitesimal size of the atom this energy is negligible, and for such a gas  $\beta$  may be taken as unity; whence, as from formula (c)  $\gamma = 1\frac{1}{2}$ .

The gases believed to be monatomic by chemists are the vapors of sodium, cadmium, zinc, and mercury. Until the discovery of argon, the only gas for which the relation above had been verified was mercury. Kundt and Warburg showed, by comparing the wave-lengths of the same sound in air and mercury vapor, that  $\gamma$  for the latter was one and two-thirds—an extraordinary confirmation of the bold speculations of Clausius.

Argon has dispelled certain beliefs in regard to monatomic gases. High boiling-points can no longer be regarded as characteristic.

Whatever nomenclature we adopt, whether we accept the ingenious suggestion of Professor Dolbear, in his "Matter, Ether, and Motion," that the internal energy of a gas is to be considered its "heat" proper, or content ourselves with Helmholtz's wider generalization of "free" and "bound" energy, the *fact* is none the less certain, that the energy of gases (monatomic excepted) exists in two distinct forms. In no other simple way can we account for the difference in the action of heat upon them—a difference directly connected in the molecular hypothesis with their complexity of constitution.

The conception of  $\beta$  as well as that of  $\gamma$  is, therefore, founded in fact.

The relations of  $\beta$  and  $\gamma$  are independent of the kinetic conception. To deduce them it is only necessary to supplement the laws of gases with two other laws, both well founded; *viz.*, Avogadro's, that equal volumes of gases under like pressure and temperature contain equal numbers of molecules, and the hypoth-

esis of Clausius that the specific heat of an atom in the (perfect) gaseous state is constant and the same for all elements. This latter hypothesis is the corner-stone of the kinetic theory in which Avogadro's law, as well as the laws of gases, is a rigid deduction.

The theoretical behavior of gases under changes of temperature, pressure, and volume, is regulated by the law of Boyle and the law of Charles. According to the first, at constant temperature the product of the pressure and volume is constant; according to the second, equal volumes of all gases expand equally under constant pressure, or show equal increments of tension at constant volume, for equal increments of temperature.

*These laws are ideal.* No gas obeys them with perfect accuracy under every condition, nor even with approximate accuracy under certain conditions. Nevertheless, they have a reality. Any one familiar with the mathematical theory of "limits" can understand their relation to the behavior of gases. We arrive at the conception of the *perfect gaseous state* in the following simple way:

If we trace the properties of a gaseous substance through a considerable range of temperature, we find that below a certain temperature, even under atmospheric pressure, the substance is a liquid. This is its boiling-point. Above this, for a certain range of temperature, although gaseous under ordinary conditions, it may be condensed into a liquid by increasing the pressure, till at length we reach a temperature above which this is impossible. This is its critical or absolute boiling-point. Above this temperature the substance is a permanent gas, but near it the gas is notably "imperfect." As we raise the temperature above this point the behavior becomes more and more nearly normal. The ideal state for every gas is, therefore, simply a question of its state of removal from the critical temperature.

#### MEASUREMENTS OF HIGH TEMPERATURES.

Temperature is the intensity factor of heat—the thermal form of energy. It is practically measured by the voluminal expansion of a standard substance. In the thermodynamic theory, it is independent of the properties of any particular substance. The absolute values of two temperatures, one higher than the

other, are to each other as the heat taken in, to the heat rejected by a perfect thermodynamic engine (with reversible cycle) working between the two temperatures as limits. The value of the degrees being fixed, this scale of temperature agrees very closely with the scale determined by the air-thermometer. It agrees perfectly with the ideal scale of perfect gases, in which equal increments of temperature correspond to equal increments of heat (mass being constant)—a principle simply expressed by saying that the specific heats are constant.

So far in science the attempts at accurate measures of high temperatures have been indissolubly connected with the increase of volume or tension of elementary gases, such as hydrogen and nitrogen. The regularity of their behavior under ordinary conditions of pressure and temperature has been checked and confirmed in various ways. Since the general effect of increasing the temperature is to correct and improve the isothermals of gases, it has been assumed that this regularity is sustained at high temperatures.

These gases have, however, a fatal theoretical defect when used as thermometrical substances at very high temperatures. Being diatomic a certain part of their energy (about 38.5 per cent.) takes the form of internal energy. This is the form in which we believe the heat exerts its decomposing influence. However this may be, these gases are theoretically subject to a gradual thermolysis or decomposition by heat. A part of the heat being rendered latent and being without effect upon the temperature, equal quantities of heat cease to correspond to equal degrees of temperature. Moreover, since in this dissociation of the molecule the specific volume is doubled, the coefficient of expansion under constant pressure or the coefficient of tension at constant volume, is changed, and the scale of temperature based upon either becomes unreliable.

Now, argon, as a thermometric substance at ordinary temperatures, has about the same properties as nitrogen or oxygen. It is a permanent gas with a low critical point— $121^{\circ}$  C. Its behavior under the usual conditions will be very similar to that of the mixture of nitrogen and oxygen we call air; its scale is therefore strictly comparable with that of the air-thermometer.

*At high temperatures it is the ideal thermometric substance.*

Neglecting dissociation, all gases improve in their behavior as the temperature rises; all discrepancies pass into the normal<sup>1</sup> which does not affect the scale of temperature of either the constant-volume or constant-pressure thermometer.

Argon has no internal energy; the decomposing influence of the heat is absent; in other words, being monatomic it cannot suffer dissociation and its behavior as a thermometric substance throughout the range of temperature will be strictly normal. No other substance has such simple heat relations over such a great range of temperature.

These theoretical considerations would seem to show that argon has great possibilities for usefulness in the hands of the skilled experimenter. In its discovery science has been given a new instrument of research. If by its use we can detect in the behavior of an elementary diatomic gas at high temperature, such an aberration as would be accounted for by the dissociation of the molecule, this will go far to confirm the conception of discrete molecules, the tenets of modern chemistry, and the kinetic theory of gases. Unless the 'molecular theory can make new conquests like these, the onward march of science bids fair to overthrow it. Already serious attacks have been made upon it, two of which have appeared in this JOURNAL, 1893, 430; 1894, 516—the brilliant papers by Prof. Trevor. While Prof. Trevor does not do the theory justice, in fact treats it very cavalierly; he is not the only thinker of the present day who has turned his back upon it. The necessity of reducing the mysterious thing we call *chemical energy* to the reign of law, has led to this estrangement. This form of energy is so obscure that we can apply to it only the most general laws of energetics. We must suppose it to consist of an intensity and a capacity factor, and to be convertible into other energy forms with a constant quantitative relation. But even these simple postulates involve us in difficulties with the molecular hypothesis. Intensity determines action. In order that two bodies may react chemically

<sup>1</sup> The normal discrepancy is as follows: All gases are compressed less under great densities and expand more under extreme rarefaction than required by the law of Boyle  $p\nu = \text{constant}$ —that is the isothermal is normal except near the extremes of pressure and volume for which the product  $p\nu$  is too large.

they must differ in chemical intensity. But what is chemical action? According to one view, it is a change in which chemical intensities are equalized, with a conversion of part of the chemical energies concerned into other energy forms; according to the other it is a union of atoms. But how can two things, which we suppose to be exactly alike, unite? Whence comes the difference of intensity? By virtue of what principle is the elementary diatomic molecule formed? If this molecule always preserved its integrity, we could regard its diatomic constitution as an elementary condition, but according to our chemical theories, the molecule in many chemical reactions is subject to division. Nevertheless, whenever the atoms are set free they combine according to the diatomic pattern.

It is thus roughly shown that the later views of chemical energy are not supported by the molecular hypothesis. Which shall we throw overboard for the sake of the other, or may we hope for a view which will embrace, possibly revise, and reconcile both?

---

## THE TUNGSTATES AND MOLYBDATES OF THE RARE EARTHS.<sup>1</sup>

BY FANNY R. M. HITCHCOCK.

Received March 2, 1895.

THE estimation of molybdic and tungstic acids, and their separation from each other have been the subject of many investigations, but notwithstanding the time and care expended the results so far attained are not perfectly satisfactory, particularly as regards their separation. The reactions which take place when either element is tested alone cannot be depended upon when the two are together, each seeming to exert some modifying action on the other.

Several years ago, Smith and Bradbury<sup>2</sup> carried out a series of experiments on the precipitation of these two acids, chiefly with salts of the heavy metals. Their research brought out many new and interesting facts relating to the precipitation and

<sup>1</sup> From the author's thesis presented to the Faculty of Philosophy of the University of Penn'a for the degree of Doctor of Philosophy, 1894.

<sup>2</sup> *J. Anal. Appl. Chem.*, September, 1891.

estimation of each acid separately, but failed to produce anything new in the way of a separation. It was with the hope that, by extending the investigation begun by them, to the action of other precipitants on these acids, additional information might be gathered which would lead to more definite results, that the experiments were undertaken, the results of which are offered in the following pages.

The molybdate solutions used in the work were made up from the sodium molybate. Analysis showed the salt to be pure and to agree with the formula given,  $\text{Na}_2\text{MoO}_4 + 2\text{H}_2\text{O}$ .

The tungstate solutions were prepared from the corresponding tungsten salt,  $\text{Na}_2\text{WO}_4 + 2\text{H}_2\text{O}$ . Analysis showed that traces of silica and ferric iron were present, and molybdenum trioxide was found to the amount of three and one-tenth per cent. This was separated by Pechard's method.<sup>1</sup>

Due allowance has been made in all calculations for the amount of molybdic acid found in the sodium tungstate.

It was found best not to prepare more than 250 cc. of the solution of sodium tungstate at one time, as on standing it gradually affects the flask, the glass being attacked, and a sediment appearing which resembles silica, and is of noticeable amount. The solution of sodium molybdate also attacked the glass, but not so strongly nor so quickly as the sodium tungstate.

#### SODIUM TUNGSTATE AND MANGANESE SULPHATE.

The solution of manganese sulphate used was a saturated one. The solution of sodium tungstate contained 27.8600 grams to the liter, and, if completely precipitated by the manganese sulphate, ten cc. of the solution should yield 0.2871 gram of manganese tungstate,  $\text{MnWO}_4$ .

The precipitates all showed the same character, however varied the conditions under which they were formed, being flocculent at first and becoming slimy on standing. They filtered very slowly and were difficult to wash.

The filtrations were made through asbestos in a Gooch crucible, and the filtrates were all tested for tungstic acid by hydrogen sulphide in ammoniacal solution, the solution being subsequently acidified with hydrochloric acid.

<sup>1</sup> *Compt rend.*, 114, 173; *Ztschr. Anorg. Chem.*, 1, 262; this JOURNAL, 15, 1, (1893).



*A. Experiment 1.*—Ten cc. of the sodium tungstate solution were diluted to 250 cc. with distilled water, brought to boiling, and fifty cc. of the manganese sulphate solution added. A voluminous precipitate formed at once, which was allowed to settle, then filtered off, washed with boiling water, dried in an air-bath at  $180^{\circ}$  C., cooled in a desiccator for three hours, and weighed.

Wt. obtained.	Wt. calculated.	Difference.
0.2310 gram.	0.2871	—0.0561 gram.

The filtrate gave a precipitate of tungsten trisulphide.

*Experiment 2.*—Ten cc. of the sodium tungstate solution were treated as before, but the precipitate was allowed to stand for two days, then filtered cold, and washed with hot water.

Wt. obtained.	Calculated.	Difference.
0.2779 gram.	0.2872	—0.0092

The filtrate gave a precipitate of tungsten trisulphide.

*Experiment 3.*—Ten cc. sodium tungstate solution were treated as before; the precipitate allowed to stand for twelve hours, then filtered cold, and washed with cold water.

Wt. obtained.	Calculated.	Difference.
0.2667 gram.	0.2871	—0.0204

*Experiment 4.*—Ten cc. sodium tungstate solution were treated as before; the precipitate was allowed to stand for twelve hours, then brought to boiling, filtered hot, and washed with a hot solution of ammonium nitrate.

Wt. obtained.	Calculated.	Difference.
0.2110 gram.	0.2871	—0.0693.

*B. Experiment 1.*—Ten cc. sodium tungstate solution were diluted to 250 cc. with distilled water, and five grams of ammonium nitrate added; the whole was then brought to boiling, and fifty cc. of the manganese sulphate solution were added; the precipitate was allowed to subside, filtered off, and washed with water containing ammonium nitrate; the filtrate was perfectly clear.

Wt. obtained.	Calculated.	Difference.
0.2351 gram.	0.2871	—0.0520

*Experiment 2.*—Ten cc. sodium tungstate solution were treated as in *B 1*. The precipitate was allowed to stand over night

before filtering, was filtered cold, and washed with cold water containing ammonium nitrate.

Wt. obtained.	Calculated.	Difference.
0.2393 gram.	0.2871	—0.0478

Both filtrates gave tungsten trisulphide.

*C. Experiment 1.*—Ten cc. sodium tungstate solution were diluted to 250 cc. with distilled water, and eighty cc. of ninety-five per cent. alcohol were added; then fifty cc. manganese sulphate solution. The solution was heated, and the precipitate formed slowly. It was voluminous, white and flocculent, becoming granular on standing; it was filtered off while still hot, washed with thirty-three per cent. alcohol, and ignited at a low temperature.

Wt. obtained.	Calculated.	Difference.
0.2666 gram.	0.2871	—0.0164

*Experiment 2.*—Ten cc. sodium tungstate solution were treated as in *C 1*. The precipitate was allowed to stand for several days before filtering, was filtered cold, and washed with thirty-three per cent. alcohol as before.

Wt. obtained.	Calculated.	Difference.
0.2707 gram.	0.2871	—0.0205

A brief inspection of the analytical results given in detail above shows beyond reasonable doubt that the precipitation of tungstic acid from its salts cannot be well hoped for when manganese salts are used as the precipitants. The most varying conditions failing to give any promise of even approximate success, further experiments with manganese salts were abandoned, and attention was turned to uranium salts. Trials were made with uranium acetate, uranyl nitrate, and uranyl chloride. With uranium acetate no precipitate formed in an aqueous solution of sodium tungstate, whether cold or hot, and an excess of either the tungstate or the acetate produced no effect. The addition of a few drops of acetic acid caused no change. Alcohol produced a slight opalescence, but though the solution stood for several days no precipitate formed. When uranyl nitrate was used a precipitate formed at once, which was pale yellow in color, flocculent, and quick to subside. The precipitation seemed to take place equally well in the presence of alcohol, and in that of ammonium salts.

The solution of sodium tungstate used contained five grams in a liter, and ten cc. would therefore yield  $0.0883 +$  gram of uranyl tungstate, if completely precipitated. The atomic mass of uranium was taken as 239.6.

A. Twenty cc. sodium tungstate solution were diluted with twenty cc. of distilled water and five cc. of a solution of uranyl nitrate added, the latter being in slight excess. This was followed by twenty-five cc. of a saturated solution of ammonium chloride, and the whole heated nearly to boiling for two hours, after which the precipitate was filtered off and washed first with water containing ammonium chloride, then with pure water. The filtration was made through Schleicher & Schull's 590 filter-paper, and the precipitate was ignited strongly with free access of air.

Wt. obtained.	Calculated.	Difference.
0.1728 gram.	0.1767	0.0039

The filtrate gave no trace of tungsten trisulphide when tested with hydrogen sulphide, and from the appearance of the precipitate after ignition some reduction had evidently taken place.

B. Twenty cc. sodium tungstate solution diluted with twenty-five cc. distilled water, were precipitated with five cc. of the uranyl nitrate solution. The precipitate was allowed to stand for one hour, was then filtered in the cold, and washed with cold water, on a tared filter which had been dried at  $150^{\circ}$  C. The precipitate was dried at the same temperature in an air-bath for two hours, and weighed at constant weight.

Wt. obtained.	Calculated.	Difference.
0.1770 gram.	0.1767	+ 0.0003

The filtrate, when tested, gave no trace of tungsten trisulphide. It may be added that when the ammonium chloride used in the first experiment was replaced by alcohol, the precipitation seemed to be equally complete, as there was no evidence of the presence of tungsten when the filtrate was tested with hydrogen sulphide.

To ascertain whether the tungstic acid could be determined volumetrically, the following experiment was made:

A solution was prepared containing fourteen grams of uranyl nitrate in one liter of water. Twenty cc. sodium tungstate solu-

tion were diluted with twenty-five cc. distilled water, and the nitrate solution introduced from a burette, the tungstate solution being constantly stirred, and the end-reaction ascertained by testing with potassium ferrocyanide on a porcelain plate.

Toward the last the reaction is rather slow, so that a brown color may be obtained with the potassium ferrocyanide before the tungsten is fully precipitated. If, however, the solution be allowed to stand a few seconds after each addition of the uranyl nitrate solution, no coloration is obtained on testing, unless the reaction is complete. By a little care the end-reaction can be made extremely close. Upon substituting a solution of uranyl chloride for the nitrate, equally good results were obtained.

#### SODIUM MOLYBDATE AND URANIUM SALTS.

A solution was prepared containing 8.51 grams of sodium molybdate to the liter, and the same salts of uranium were tried that had been used in the experiments with tungstic acid.

With uranium acetate, sodium molybdate behaved similarly to sodium tungstate, no precipitate being obtained by any method tried. With the nitrate of uranium, however, a precipitate is formed at once which redissolves on stirring, though not completely, a small quantity of some flocculent material remaining undissolved; boiling did not bring down any further precipitate, and an excess of the nitrate had no effect. The uranyl nitrate solution was the same as that used with sodium tungstate, and contained fourteen grams to the liter. On trying a concentrated solution of uranyl nitrate a dense precipitate formed at once, which, on dilution, dissolved in part, but very imperfectly.

Addition of alcohol does not change the behavior in either a cold or a hot solution.

A solution containing twenty-five cc. of a saturated solution of ammonium chloride, twenty cc. of the sodium molybdate solution, and twenty-five cc. of water gave no permanent precipitate with uranyl nitrate, but when twenty cc. of the sodium molybdate solution were diluted with twenty-five cc. water, and the uranyl nitrate solution added in excess, the addition of ammonium chloride brought down the whole of the molybdenum.

With uranyl chloride, a precipitate was obtained at once,

which, like that produced by uranyl nitrate, redissolved on stirring, as fast as it formed.

On standing, a pale lemon yellow precipitate appeared, which on heating went into solution. With the addition of an excess of uranyl chloride to the cold solution, a precipitate forms similar in appearance to the one just described, but on heating it does not redissolve. Heated for an hour it grows denser, and gradually becomes crystalline. These crystals are insoluble in water, and those which I obtained were washed first by decantation, then on the filter with cold water, dried on the air-bath at  $128^{\circ}\text{C}$ . (without any alteration in appearance), and analyzed.

The molybdic acid was determined by heating the salt in a current of hydrogen chloride gas. The  $\text{MoO}_3 \cdot 2\text{HCl}$  came off readily at a low heat, the salt in the boat changing in color from a brilliant golden yellow to a light green, then to a golden brown, and finally to a dark green, almost to a black.

This blackish residue when treated with concentrated hydrochloric acid did not dissolve; with aqua regia it did slowly dissolve to a deep yellow solution from which the uranium was precipitated by ammonium hydroxide; the precipitate after strong ignition had a metallic appearance. It was dissolved in concentrated nitric acid, evaporated to dryness, and gradually heated to a dull red heat. The brownish yellow powder obtained was weighed as uranium trioxide.

A slight loss occurred when the salt was heated in the stream of hydrogen chloride gas, as a little was carried over mechanically, and heated so strongly to the walls of the tube that it could not be removed.

The weight of material taken for analysis was one-tenth of a gram. The weights obtained were as follows:

Molybdenum trioxide = 0.0333 gram = 33.3 per cent.

Uranium trioxide = 0.0620 gram = 62.0 per cent.

These values correspond very closely to the formula  $\text{UO}_2 \cdot \text{MoO}_3$ , when the radicle  $\text{MoO}_3$  may be regarded as replacing the two chlorine atoms in the uranyl chloride. The theoretical amounts required for this formula are

Molybdenum trioxide = 0.0334 gram = 33.4 per cent.

Uranium trioxide = 0.0666 gram = 66.6 per cent.

Water of crystallization does not seem to be present; one-tenth of a gram of the substance was dried over sulphuric acid for two days, and then in the air-bath for two hours at a temperature of  $128^{\circ}\text{C}$ . The loss in weight was eight-tenths of a milligram. On strong ignition the color changed at first a light green, then to a golden brown, and on cooling became once more bright yellow. By this ignition a loss in weight occurred amounting to nine and three-tenths milligrams; a second ignition caused no further loss.

Both before and after ignition the salt is readily soluble in hydrochloric acid, apparently without decomposition, as no reaction for uranium is given by the solution when tested with potassium ferrocyanide.

The perfect precipitation of tungstic acid by uranyl nitrate from the sodium tungstate solution, and the non-precipitation of molybdic acid by the same reagent, encouraged a hope that a separation of the two acids might be possible through its means.

As potassium ferrocyanide indicated the end reaction so sharply between sodium tungstate and uranyl nitrate, some tests were made with it as an indicator, with solutions of sodium molybdate and uranyl nitrate. Observing the same precautions as before the end reaction was equally sharp. It was observed, however, that the red color imparted to the potassium ferrocyanide by a drop of the molybdate solution as soon as the uranyl nitrate was in excess, gradually disappeared, and was not restored by the further addition of uranyl salts. The conditions were next varied by introducing the potassium ferrocyanide into the molybdate solution instead of making the tests on a porcelain plate as heretofore. Twenty cc. of sodium molybdate were diluted with twenty-five cc. of water, and five cc. of potassium ferrocyanide added. The uranyl nitrate solution was then run in, the red color appearing when 33.3 cc. of the uranyl nitrate had been used; an excess of six or seven cc. were added, and a deep red solution formed, but no precipitate appeared. After standing for two hours the red color had disappeared, and the solution had become yellow. A portion of this was tested with potassium ferrocyanide, but no reaction was obtained for uranium.

The addition of uranyl nitrate to another portion showed no excess of the potassium ferricyanide. On substituting uranyl chloride for the nitrate the red solution was not obtained, but a reddish brown precipitate came down which was much lighter in color than that given by the uranyl salts alone.

Twenty cc. sodium tungstate solution were mixed with five cc. of the sodium molybdate solution, and diluted with twenty-five cc. of water; the uranyl nitrate solution was next run in from a burette, and the end reaction ascertained by potassium ferrocyanide on a porcelain plate. After standing for an hour the precipitate was filtered off in the cold, and washed with thirty-three per cent. alcohol.

It was hoped that the filtrate would contain the molybdenum, but examination showed that the greater part of it had been precipitated with the tungsten.

A second solution was prepared and titrated in the same manner as before; the precipitate with the supernatant fluid was then heated for an hour at a temperature of 60° C., filtered while hot, and washed with hot water containing thirty-three per cent. of alcohol. The molybdic acid was found in both filtrate and precipitate, though more went into the filtrate than in the first case.

On substituting uranyl chloride for the nitrate and repeating the titration, only a slight precipitate of the tungsten formed, the greater part dissolving with the molybdate, as fast as formed.

An excess of uranyl chloride brought down both the tungsten and the molybdenum completely. It was evident that no separation could be hoped for by means of uranium salts. There seems to be a tendency on the part of the members of the chromium sub-group to form compounds with each other which are not readily broken up, and which probably contain complex radicles of as yet unknown constitution. This is very strongly indicated by the behaviour of molybdic acid with uranyl salts, and the failure of the resulting compound to react in solution, for uranium with potassium ferrocyanide.

As the chief object of my investigations was to ascertain the manner in which the rare earths would act with tungstates and

molybdates, these were now taken up and studied in detail. As the quantity at my disposal of any one of the rare earths used was necessarily very limited the material had to be worked over frequently, and a great deal of time was in consequence consumed by this preparatory work.

#### SODIUM MOLYBDATE AND CERIUM SULPHATE.

The solution of sodium molybdate used contained 13.24 grams to the liter, so that ten cc. of the solution should give 0.1628 gram of cerium molybdate,  $Ce_2(MoO_4)_3$ , if fully precipitated. The solution of cerium sulphate used was saturated.

*Experiment 1.*—Five cc. of the sodium molybdate solution were diluted to 150 cc. with distilled water, and ten cc. of the cerium sulphate solution added in the cold. A voluminous, white gelatinous precipitate formed at once. This stood for eighteen hours, when it had become granular in appearance and was yellow in color. It was filtered cold, washed with cold water, ignited and weighed. The theoretical weights are all calculated for the formula  $Ce_2(MoO_4)_3$ .

Wt. obtained.	Calculated.	Difference.
0.0760 gram.	0.0814	—0.0054

*Experiment 2.*—Five cc. of the sodium molybdate solution diluted to 150 cc. with distilled water were brought to boiling, when ten cc. of the cerium sulphate solution were added. A white precipitate formed at once, soon becoming curdy, and then granular, the color changing to yellow. This was allowed to stand for twelve hours, was then filtered, and washed with hot water, ignited and weighed.

Wt. obtained.	Calculated.	Difference.
0.0752 gram.	0.0814	—0.0062

*Experiment 3.*—Ten cc. sodium molybdate solution were diluted to 500 cc. with distilled water, and fifteen cc. of the cerium sulphate solution added in the cold. The precipitate after standing for twelve hours was filtered on asbestos in a Gooch crucible, ignited and weighed.

Wt. obtained.	Calculated.	Difference.
0.1596 gram.	0.1629	—0.0033

*Experiment 4.*—This was a duplicate of No. 3, excepting that the filtration took place as soon as the precipitate had settled.

Wt. obtained.	Calculated.	Difference.
0.1555 gram.	0.1629	—0.0074



From both filtrates additional precipitates were obtained on boiling.

*Experiments 5 and 6.*—Ten cc. of the sodium molybdate solution were diluted to 110 cc. with distilled water and brought to boiling, when fifteen cc. of the cerium sulphate solution were added; after two hours the precipitate was filtered off, washed with hot water, ignited and weighed.

	Wt. obtained.	Calculated.	Difference.
5.	0.1496 gram.	0.1629	—0.0133
6.	0.1587 "	0.1629	—0.0042

*Experiment 7.*—Ten cc. sodium molybdate solution were diluted to 110 cc. with distilled water, fifteen cc. of cerium sulphate solution added in the cold, and the whole brought to boiling, when twenty-five cc. of ninety-five per cent. alcohol were added. The precipitate was filtered off through Schleicher and Schull's 590 filter-paper, washed with fifty per cent. alcohol, ignited and weighed.

	Wt. obtained.	Calculated.	Difference.
	0.1583 gram.	0.1629	—0.0041

*Experiment 8.*—Ten cc. of sodium molybdate solution were diluted to 110 cc., fifteen cc. of cerium sulphate solution added in the cold, the whole brought to boiling, when one-third the volume of ninety-five per cent. alcohol was added. The precipitate stood for twelve hours before filtering; it was apparently not homogeneous, as a fine white powder was mixed through the yellow cerium molybdate. The filtering was very slow, and the washing with fifty per cent. alcohol was continued for two days.

	Wt. obtained.	Calculated.	Difference.
	0.2118 gram.	0.1629	+0.0489

*Experiment 9.*—Ten cc. sodium molybdate solution were diluted to 100 cc. and fifteen cc. cerium sulphate solution added in the cold, followed by one-third the volume of ninety-five per cent. alcohol. The precipitate was filtered after standing for two hours, and like that in No. 8, was not homogeneous in appearance.

	Wt. obtained.	Calculated.	Difference.
	0.1919 gram.	0.1629	0.0290

*Experiment 10.*—Ten cc. of sodium molybdate solution were diluted to 100 cc., and fifteen cc. cerium sulphate solution added.

The whole was boiled for an hour, allowed to cool, when one-third the volume of ninety-five per cent. alcohol was added. After standing twelve hours, it was filtered, washed with fifty per cent. alcohol, ignited and weighed.

Wt. obtained.	Calculated.	Difference.
0.2156 gram.	0.1629	0.0497

The precipitates from 8, 9 and 10, after ignition, were dissolved in hydrochloric acid, and tested with barium chloride; all gave precipitates of barium sulphate, as was expected. The following experiments were then made to determine what proportion of alcohol could be added without causing the cerium sulphate to precipitate.

a. Five cc. of the cerium sulphate solution were diluted to sixty cc., then twenty cc. of ninety-five per cent. alcohol were added in the cold, and, no precipitate forming, more alcohol was added, five cc. at a time, until seventy cc. in all had been introduced. The solution still remained perfectly clear.

[TO BE CONTINUED.]

## SOME NEW LABORATORY APPARATUS.

BY EWALD SAUER.

Received January 31, 1895.

### I. HOT AIR MOTOR FOR LABORATORY PURPOSES.

**I**N laboratories mechanical power is desirable for many undertakings which require continued shaking and stirring of liquids, as well as for rotation and grinding. While the factory steam-engine furnishes usually the necessary power for the laboratory of the technical chemist, nevertheless it is often desirable to have a separate source of power in case, for instance, of this not being in use.

For this purpose the turbines constructed by Raabe<sup>1</sup> have proved themselves useful in certain kinds of work, but only when small power is required. For many purposes the power is too weak, *e. g.*, the shaking of large quantities of liquids and the stirring of thick liquids.

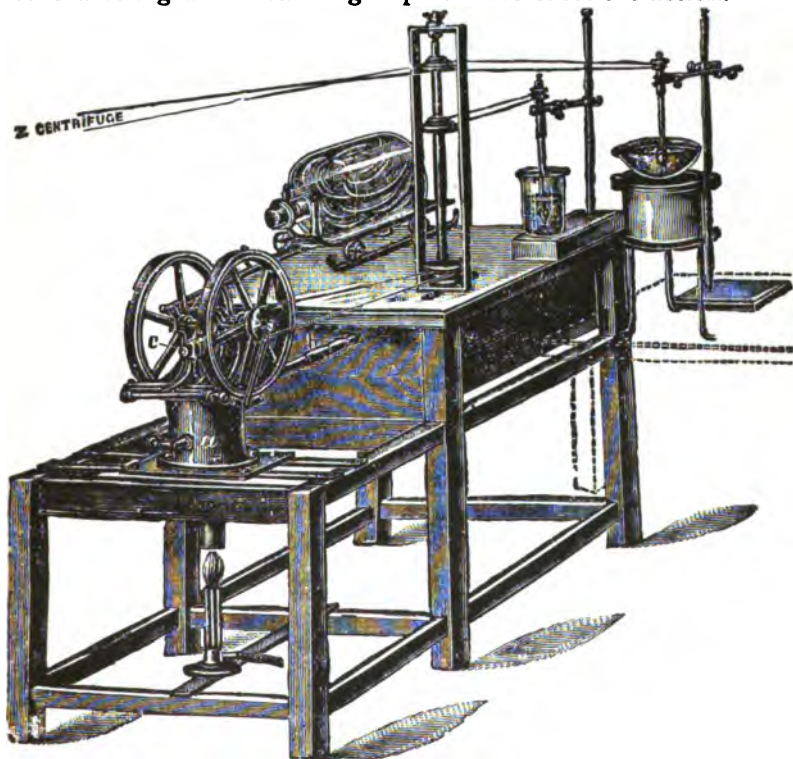
The hot air motor of Heinrici, which is pictured below, and which has already proved of practical value in several labora-

<sup>1</sup> *Ber. d. chem. Ges.*, 1888, p. 1200.

tories, would in most cases furnish abundant power for the different kinds of work.

The motor is built according to the well-known principle of hot air machines, so that its use is absolutely free from danger. It may be heated by gas, petroleum, etc. The more intense the source of heat, the more power the machine furnishes, and if the fire-pot be red hot beneath, the motor furnishes the most power.

About two minutes after the burner heats the pot the motor begins its action. There must be a space of about ten mm. between the burner and pot. A brake upon the fly-wheel regulates the speed of the machine, or brings it to a standstill. While in use, cold water must circulate through the motor, otherwise a gradual warming of part *a* decreases the action.



In the accompanying illustration, the cooling reservoir is

contained in the table, and the circulation of water takes place through the tube *b*. Where a water system is available the body of the motor may be fastened directly in the table by its support.

On the table is fastened a carriage, upon which bottles up to six liters capacity may be shaken vigorously to and fro. The action is most satisfactory with such large quantities.

Should it be desired to shake, at the same time, several bottles of smaller capacity, wooden boxes may be fastened on the carriage, which is partitioned and so arranged that each vessel may be easily made firm.

An axle, fastened on the table, receives the belt-cord coming from the motor and is furnished with two movable wheels which furnish connections with Witt's centrifugal stirrers for stirring, evaporating, etc. These stirrers, held as nearly perpendicular as possible in a nickel cylinder, and properly connected with the motor, act in a highly satisfactory manner.

## II. ILLUMINATING APPARATUS AFTER A. LUPP.

This serves for the precise determination of the end-reaction in volumetric analysis, especially in acidimetry and alkalimetry in general, in all quantitative determinations, in which changes of color of the indicator (litmus, turmeric, cochineal, etc.) determines the analysis.

The apparatus consist of a tripod, under which a concave mirror is placed at a fixed angle.

By means of this, the sun's rays are concentrated, and so reflected as to pass through the bottom of the beaker, which is placed on the apparatus, through the solution to be titrated to the surface. Since, by means of the apparatus the titration is seen from above, one can, even in *cloudy* weather, always determine exactly the end-reaction because the liquid under examination is always strongly illuminated.

The illuminating apparatus is further adapted to enable one to recognize very fine colored precipitates or colorations, for example, in water analysis reaction for iron by means of potassium ferro- and ferricyanide, and potassium thiocyanate, etc. One needs only to hold a test-tube over the apparatus in order to recognize the slightest trace of a color or precipitate.

## NEW BOOKS.

HANDBUCH DER STEREOCHEMIE. UNTER MITWIRKUNG VON DR. PAUL WALDEN, PROFESSOR DER PHYSIKALISCHEN UND ANALYTISCHEN CHEMIE AM POLYTECHNIKUM ZU RIGA HERAUSGEGEBEN VON DR. C. A. BISCHOFF, PROFESSOR DER ALLGEMEINEN CHEMIE DASSELBST. 1060 Seiten und 250 Abbildungen. Frankfurt am Main: H. Bechhold. 1893-4. Price, 34 m.

In 1880, when the writer of this notice attended the most comprehensive course of lectures on organic chemistry at that time given in America, the lecturer devoted a portion of one hour to the subject of "Physical Isomerism." The theory of the asymmetric carbon atom, proposed almost simultaneously by van 't Hoff and Le Bel in 1874, was alluded to as offering a possible explanation of the opposite rotatory powers and the enantiomorphism of the tartaric acids, and was illustrated by two simple tetrahedral models. Nothing more was said, or could well have been said on the subject. At that time the paradoxical isomerism of fumaric and maleic acids was explained by supposing the latter to contain a carbon atom with free bonds, an assumption totally without experimental justification. Attempts to give structural formulas to the rapidly increasing number of isomers among the crotonic and cinnamic acids and allied bodies resulted only in the worst kind of confusion, and it gradually became evident that either the theory of structure was insufficient or the usual experiments relied on to establish the formulas were worthless. By 1887 a large division of organic chemistry was in an almost chaotic condition. The views of van 't Hoff and Le Bel had received but slight consideration, apparently for no other reason than that chemists had concluded that it was impossible to learn anything about the geometrical arrangement of atoms, and therefore that all attempts to explain phenomena on such hypotheses must be worthless. In this year Wislicenus, who had been one of the few to appreciate the possibilities of a "chemistry in space," published his pamphlet, *Ueber die räumliche Anordnung der Atome in organischen Molekulan*. The appearance of this work marks a point in the development of chemistry of equal or even greater importance than the announcement of the benzene theory by Kekulé; less than eight years have passed, and already the geometry of molecules has become the leading

idea in organic chemistry, to the study of which many of the best workers in the organic field are devoting themselves. How long an idea prematurely born may lie dormant is here well illustrated, Wollaston having in 1808 clearly stated the conception of a tetrahedral arrangement of four atoms about a fifth.

How fruitful the new theory has been, it needs only an inspection of the present book to see. A volume of over a thousand pages is largely devoted to the consideration of isomers which can be explained on the hypothesis of geometrical isomerism, and which cannot be explained on any other which has been proposed, and certainly not on the older conceptions of structure. The remarkable discovery of the isomeric cyclohexane derivatives by von Baeyer, and the brilliant work of Fischer on the carbohydrates are not only the direct offspring of this theory, but would have been impossible without it. One of the most striking evidences of rapid progress is that although the two sections of the *Handbuch* appeared in two successive years, the second has appended a supplement of nearly 200 pages, most of which was required to bring the work up to date.

Although the book is divided into a *general introduction* and a *special part*, the reader would err in supposing the latter to be of importance for the specialist only; it contains quite as much of general and theoretical interest as the former. The *general part* (134 pages) is devoted to an historical review of the subject, and in it may be found about every attempt to explain chemical phenomena by space relations. Of the *special part* the first section (296 pages) is devoted to the relation of stereochemical theories to the optical rotation of organic compounds, with a consideration of nearly all known cases. The proteids are omitted, as their chemical nature is not sufficiently understood. The second section (204 pages) treats of geometrical isomerism in a wider sense, and describes all compounds to which the theory may apply, whether they are at present known in more than one form or not, as well as those which while existing in several forms, cannot be explained by the theory as at present developed. The stereochemistry of nitrogen, as exhibited in the oximes and other bodies is fully treated. Both the older nomenclature and that of the Geneva Congress are used, and the classification is the purely artificial, but extremely convenient one used by Richter in his

*Tabellen der Kohlenstoffverbindungen.* The third section includes a chapter on the formation of rings (124 pages) which while not properly a part of stereochemistry, is valuable as containing a diagram of every kind of ring discovered or supposed to exist, into which carbon enters, as well as many wholly inorganic rings. One wonders what Kolbe would say about the hexa- and hepta-cyclic systems, were he now living. But little is said of the reactions by which these rings are formed, or of the proofs of their structure, but there are full references, which take the place of a broader discussion. This chapter forms a complete "Handbuch der Ringschliessung." Anyone looking up the various benzene theories will find in this work a good directory. The chapter on rings is followed by others on intramolecular transpositions, addition and splitting off of atoms and groups, and the limits of general reactions, in as far as these may be supposed to be influenced by the geometrical structure of the molecule. These constitute one of the most valuable and interesting parts of the work.

The authors are to be commended for having given considerable space to inorganic compounds. Not much was to be said on the subject, as it is still in its infancy; the inorganic ring systems which have an experimental warrant are as yet but few, and these of the simplest nature, and with the exception of a few observations and speculations on sulphur and ammonia derivatives we have yet to see the beginning of a stereochemistry of inorganic bodies. We regard inorganic structure and stereochemistry a promising field for investigators who do not believe that all the laws of chemistry worth knowing can be discovered by the study of carbon compounds only, and who have the courage to strike out in new lines, and the patience to search for new methods. With the view of aiding such pioneers the authors have given in a special chapter a list of inorganic substances occurring in more than one form, which will prove of value to investigators in this field. The list makes no pretension to completeness; we miss, for example, the metaphosphoric acids, some of which may in future prove to be stereoisomers.

A knowledge of stereochemistry has already become essential to a scientific understanding of the carbohydrates, and there are indications that it will play an important part in the chemistry

of fermentation and of the physiological processes. To those who are interested in these branches, as well as to the working organic chemist, and the teacher who is called on to give more than a bare outline of the subject, as well as to every one who wishes to keep up with the development of the science, this work may be heartily recommended. H. N. STOKES.

**A TEXT-BOOK OF ORGANIC CHEMISTRY.** BY A. BERNTHSEN, PH. D., DIRECTOR OF THE SCIENTIFIC DEPARTMENT IN THE CHIEF LABORATORY OF THE BADEN ANILINE AND ALKALI MANUFACTORY, LUDWIGSHAFEN-AM-RHEIN; FORMERLY PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF HEIDELBERG. TRANSLATED BY GEORGE MCGOWAN, PH. D. pp. 596. New York: D. Van Nostrand Co. 1894. Price, \$2.50.

This book is a translation of the fourth German edition, appearing as the second English edition. The usefulness of Dr. Bernthsen's work is indicated by the fact that the fourth edition is called for within the brief space of six years. A comparison of the former and present editions impresses one with the tremendous activity and rapid development that have been going on recently in this field of chemical research. While this edition follows closely the plan of the previous ones, every part has been carefully revised and several chapters have been entirely rewritten, in order to present the most recent knowledge about the subjects considered. Among such specially revised subjects may be mentioned the following: stereochemical isomerism; the determination of molecular weights by physical methods; aldoximes and ketoximes; carbohydrates; ketonic acids, di-ketones, etc.; special benzene formulas; aromatic compounds of phosphorus, etc.; hydrogenized phthalic acids; dyes of the diphenylene-methane oxide, phenazine, oxazine, and thiazine groups; certain naphthalene derivatives; the quinoline and acridine groups; alkaloids, especially the derivatives of tropine; the terpenes and camphors. The system of international nomenclature adopted at the recent Geneva convention of chemists is used in connection with the former names. The book, as a whole, can well be pronounced a comprehensive embodiment of our present knowledge of the essential facts and theories of the organic chemistry of to-day. The author has made a very judicious use of references to original articles which have a historic value. There is a valuable index of nearly thirty pages.



While this book is intended primarily for the use of students, it can hardly be recommended as a desirable work for those just entering upon the study of organic chemistry, since it is much too full for such. It will be found most helpful to those who have such a knowledge of the subject as can be obtained from a work like Remsen's little book on organic chemistry. It will also be a most grateful help to those who are engaged in various lines of chemical work and who desire to keep informed of the present state of knowledge of organic chemistry, but who have not time or means to get their knowledge at first hand from the literature of the various chemical journals. L. L. VAN SLYKE.

MANUAL OF CHEMISTRY. BY W. SIMON, PH.D., M.D., ETC. Fifth Edition. pp. 502. Lea Bros. & Co. 1895.

Professor Simon has found it desirable to issue a revised edition of what is correctly termed a manual of chemistry. When to the title is added that it is especially a manual for medical students, the experienced reader knows tolerably well what advantages and shortcomings are to be looked for; and if the reviewer adds that the advantages are well represented, and the shortcomings are such as are identical to the plan of the book, it will be easy to form a general idea of its character.

The first fifty pages go over the theory of chemistry from the most elementary definitions to a discussion of the periodic law. Now it is manifestly impossible to give in a couple of hours' reading a satisfactory treatise on such a subject. On the other hand, it is desirable for medical students to have some knowledge of chemical theory; and as the medical student's chemical library consists too often of but one book, it is necessary to put the main facts in that book. It is, of course, understood that the book is to be supplemented by an extended course of lectures, and is intended to give, first, elementary knowledge to the young student, and second, a repository of all the principal things he subsequently learns, for future reference. Now this book gives these things very well indeed; and what has been said of the theoretical part applies to the whole book. It goes into descriptive chemistry, and analysis, qualitative and quantitative, and physiological chemistry, and treats of all the chemicals men-

tioned in the U. S. Pharmacopeia. Happily it was not thought best to include industrial chemistry.

The book is concisely written in good English, and is embellished with eight colored plates, representing sixty-four reactions very useful to the student, and by no means easy to produce; they seem very good.

A. H. SABIN.

### NOTES.

*Note on a Molding-sand.*—A number of years ago a bed of excellent molding-sand was discovered in Belmont County, Ohio, near the Ohio river. It was, in fact, pronounced almost an ideal sand for heavy castings, and so popular was it with foundrymen, that the bed is now about exhausted, and has been closed by the owner.

The sand, when taken from the bed, coheres in lumps, is dark colored and rather coarse-grained. The grains consist of a rounded quartz nucleus, covered with a coating of brownish-red clay, that seems to adhere closely to the quartz, but dissolves when the sand is treated with hydrochloric acid, leaving the pure white nucleus behind.

The sand, even when rammed in a mold, is very porous, readily permitting the escape of gases, it is strongly cohesive, and will not blister or scale off when the molten metal flows over it. Most sands used for making heavy castings soon have the life burnt out of them; but it is said that this sand is wonderfully tough and durable.

Few sands possess, along with other good qualities, this desideratum of life-length.

Whether the good qualities of this particular sand are due to its physical condition, or to its chemical composition, or, as seems likely, to both, the writer cannot say.

An analysis of the sand, dried at 100° C., follows:

Free silica .....	73.47	per cent.
Combined silica.....	5.30	" "
Alumina .....	12.86	" "
Ferric oxide.....	3.97	" "
Lime.....	0.62	" "
Magnesia.....	0.60	" "
Organic and water .....	3.13	" "

Total..... 99.95









1

